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TOMUS IX



FASCICULI 3-4

SZEGED, HUNGARIA
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GYULAI J., GALIBA I. és HALMOS M.

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EXPERIMENTELLE UNTERSUCHUNGEN ÜBER DEN ZUSAMMENHANG DER GESETZE VON FLUORESZENZ UND TEMPERATURSTRAHLUNG

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(Eingegangen am 15. Juni 1963)

Es wird die Gültigkeit der Stepanowschen Formel experimentell untersucht. Die Meßergebnisse zeigen, daß die spektrale Verteilung der Temperaturstrahlung der Lösungen Abweichungen von dem Fluoreszenzspektrum aufweist.

§ 1. Zur experimentellen Unterstützung der bei den kondensierten lumineszierenden Systemen geltenden STEPANOWSchen Relation [1]

$$\frac{f_e(\nu)}{k(\nu)} = D\nu^3 e^{-\frac{h\nu}{kT}} \quad (1)$$

bzw. deren modifizierten Form [2]

$$\frac{f_e(\nu)}{k(\nu)} = Dn^2(\nu)\eta(\nu)\nu^3 e^{-\frac{h\nu}{kT}} \quad (2)$$

wurden bereits mehrere Untersuchungen [3–8] durchgeführt ($f_e(\nu)$ bezeichnet das Lumineszenzspektrum, $k(\nu)$ das Absorptionsspektrum, D eine von der Frequenz ν unabhängige Konstante, T die absolute Temperatur der Lösung, $n(\nu)$ den Brechungsindex, $\eta(\nu)$ die Quantenausbeute, h bzw. k die Planck'sche bzw. die Boltzmann'sche Konstante).

Jedoch genügen die zur Verfügung stehenden Versuchsdaten nicht um einzelne bei der Untersuchung der Gl. (1) und (2) auftretenden Fragen beantworten zu können.

Deshalb wurden Messungen an Lösungen mehrerer Stoffe von verschiedener Struktur durchgeführt, bei denen das Maximum des Lumineszenzspektrums an verschiedenen Stellen des sichtbaren Spektralgebietes liegt.

Die auf die Gültigkeit der Gl. (1) bezüglichen Untersuchungen wurden zum Teil mit den bereits von anderen Autoren angewendeten Methoden durchgeführt. Falls Gl. (1) erfüllt ist, soll die Darstellung des Zusammenhanges

$$F(\nu) = \lg f_e(\nu) - \lg k(\nu) - 3 \lg \nu \quad (3)$$

als Funktion der Frequenz ν eine Gerade ergeben, deren Steigung m die Berechnung der „effektiven Temperatur“ T^* der Lösung ermöglicht (nach Gl. (1) sollte

$m = -(h \lg e)/kT$ sein, doch ergibt sich aus dem bisherigen Untersuchungen $m = -(h \lg e)/kT^*$, wo T^* die „effektive Temperatur“ der Lösung bedeutet). Die logarithmische Auswertungsmethode (3) ist aber nicht empfindlich genug, deshalb schien es angezeigt, den Zusammenhang der Spektren auch auf eine andere Weise zu untersuchen.

Aus Gl. (1) geht hervor, daß das Lumineszenzspektrum $f_e(\nu)$ und der zur Temperatur T gehörende Emissionskoeffizient $W_e^T(\nu)$ der Temperaturstrahlung (die Planck'sche Funktion ϵ_ν einander proportional sind:

$$f_e(\nu) = D(T)W_e^T(\nu) \quad (4)$$

Gl. (2) ergibt dagegen den Zusammenhang

$$f_e(\nu) = D(T)\eta(\nu)W_e^T(\nu). \quad (5)$$

Im weiteren wird die Gültigkeit der Zusammenhänge (3) und (4) eingehend untersucht.

§ 2. Die Absorptionsspektren der Lösungen wurden mittels eines Spektrophotometers Optica Milano Typ CF—4 untersucht, bei dem — mit Hilfe einer zusätzlichen Einrichtung — die Schichtdicke der Lösungen bis zu 20 cm erhöht werden konnte. Die Ausmessung der Lumineszenzspektren erfolgte mit der in [9] beschriebenen Methode. Die Reabsorption wurde stets berücksichtigt, während die Spektrale Wirkung der Sekundärlumineszenz durch die Herabsetzung der Schichtdicke l der zu messenden Lösung unter die Fehlergrenze der Messung gebracht wurde [9]. Als Lichtquelle diente eine Xenonlampe Osram XBO 500 bzw. eine Quecksilberlampe HBO 200 derselben Fabrik. Das erregende Licht wurde mittels eines Doppelmonochromators oder eines Interferenzfilters SIF nahezu monochromatisiert. Die auf die Lösungen und die Versuchsbedingungen bezüglichen Daten sind in Tab. I zusammengefaßt.

§ 3. Aus den in Fig. 1—9 dargestellten Absorptions- und Lumineszenzspektren läßt sich die qualitative Gesetzmäßigkeit ablesen, daß *die als Funktion der Wellenlänge λ dargestellten Spektren einander um so mehr überlappen und in Überlappungsgebiet einen um so steileren Verlauf aufweisen, je größer die dem reinen Elektronenübergang entsprechende Wellenlänge ist.*

In Fig. 10 wurden die der Gl. (3) entsprechenden Geraden dargestellt (die auf die einzelnen Stoffe bezüglichen Zahlen bei den Kurven entsprechen den Nummern der Tab. I). Aus der Figur geht hervor, daß Gl. (3) im Falle von acht untersuchten Lösungen erfüllt ist, auf die Erythrosin—Lösung dagegen nicht anwendbar erscheint. (Im letzterwähnten Falle ist wahrscheinlich die in [2] eingeführte Bedingung 1 oder 7 nicht erfüllt.) Die in Spalte 11 der Tab. I enthaltenen, aus der Steigung der Kurven berechneten Werte T^* , deren Fehler höchstens 2—5 °K beträgt, sind in jedem Falle höher, als die wahre Temperatur T der Lösungen. Die Temperaturunterschiede $\Delta T = T^* - T$ zeigen, wie aus der Tabelle ersichtlich, weder mit der spektralen Lage des Lumineszenzspektrums, noch mit der absoluten Quantenausbeute der Fluoreszenz einen eindeutigen Zusammenhang.

Zur Kontrolle der Formel (1) mit der nichtlogarithmischen Methode auf Grund der Gl. (4) wurden in Fig. 11 die Lumineszenzspektren für fünf Stoffe mit ausgezogenen Linien dargestellt (die Nummern der Kurven entsprechen denjenigen der Tabelle I). Die gestrichelten Kurven beziehen sich auf die Funktionen $W_q^T(\lambda)$,

Tabelle 1

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|-----|--|---|--|-----------|---|----------------------|---|-----------|-----------------------------|--|
| Nr. | Fluoreszierende Stoffe und Konzentrationen (Mol/l) | Lösungsmittel und Zusätze | Angaben zur Bestimmung der Quantenausbeute | | | | Angaben zur Bestimmung des Lumineszenzspektrums | | | |
| | | | λ_e in m μ | I in cm | $k(\lambda)$ in cm $^{-1}$ $k_{\max}(\lambda) \cdot I$ | $\eta(\lambda)$ in % | λ_e in m μ | I in cm | $k_{\max}(\lambda) \cdot I$ | $T \cdot K^\circ$ ($T = 298^\circ K$) |
| 1 | Äsculin $5 \cdot 10^{-5}$ | Äthanol $5 \cdot 10^{-3}$ Mol/l NaOH | 407 | 0,05 | 1,659 0,08295 | 98 | 409 | 0,01 | 0,01659 | 325 |
| 2 | Al-Morin $5 \cdot 10^{-5}$ | Äthanol 1 Vol% CH_3COOH | 430 | 0,06 | 2,312 0,1387 | 97 | 420 | 0,05 | 0,11560 | 329 |
| 3 | Trypaflavin $5 \cdot 10^{-5}$ | Äthanol $3 \cdot 10^{-3}$ Mol/l HCl | 460 | 0,02 | 5,957 0,1191 | 70 | 436 | 0,01 | 0,0596 | 344 |
| 4 | Fluoreszein $5 \cdot 10^{-5}$ | Wasser 3% NaOH | 490 | 0,01 | 10,35 0,1035 | 93 | 475 | 0,01 | 0,1035 | 316 |
| 5 | Rhodulinorange $5 \cdot 10^{-5}$ | Äthanol $3 \cdot 10^{-3}$ Mol/l NaOH | 491 | 0,05 | 2,356 0,1178 | 81 | 483 513 | 0,05 | 0,1178 | 321 |
| 6 | Eosin $5 \cdot 10^{-5}$ | 20% Wasser + 80% Äthanol $5 \cdot 10^{-3}$ Mol/l NaOH | 520 | 0,01 | 26,48 0,2648 | 93 | 505 530 | 0,001 | 0,02648 | 350 |
| 7 | Erythrosin $5 \cdot 10^{-5}$ | Äthanol $5 \cdot 10^{-3}$ Mol/l NaOH | 520 | 0,01 | 13,60 0,1360 | 83 | 505 530 | 0,01 | 0,1360 | — |
| 8 | Rose Bengale $5 \cdot 10^{-5}$ | Äthanol $5 \cdot 10^{-3}$ Mol/l NaOH | 552 | 0,06 | 7,650 0,459 | 30 | 546 | 0,05 | 0,38250 | 395 |
| 9 | Rhodamin B $5 \cdot 10^{-5}$ | Äthanol $5 \cdot 10^{-3}$ Mol/l HCl | 555 | 0,01 | 9,898 0,0989 | 57 | 546 436 | 0,01 | 0,0989 | 328 |

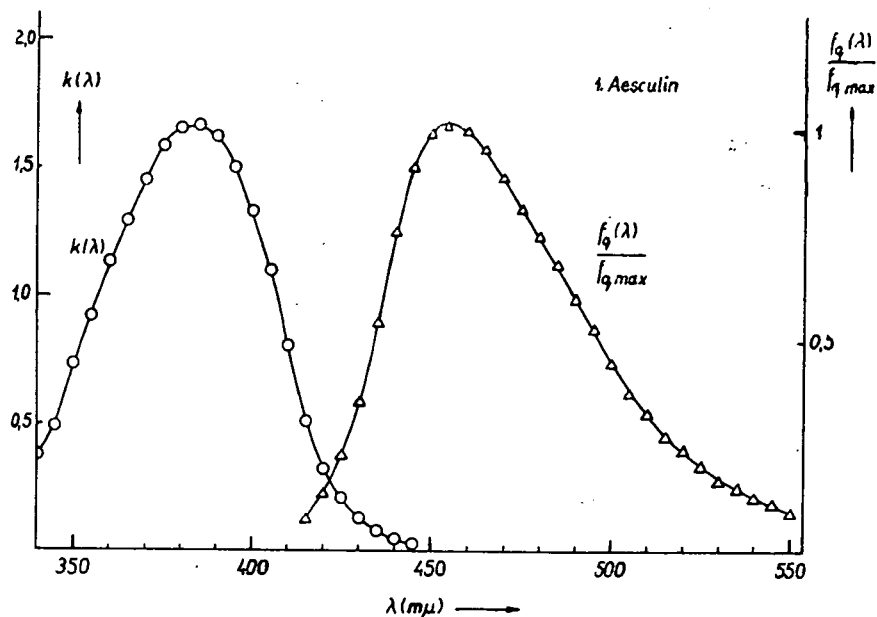


Fig. 1

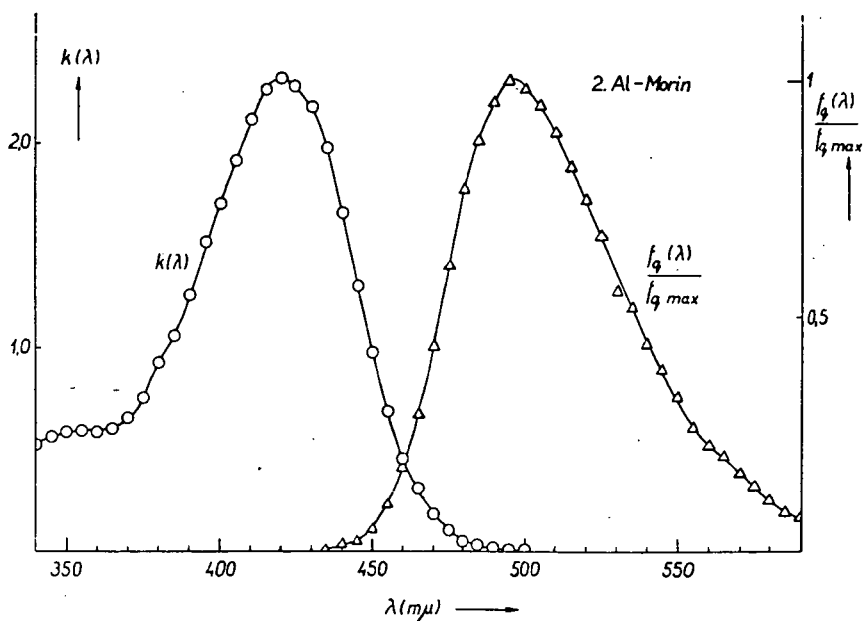


Fig. 2

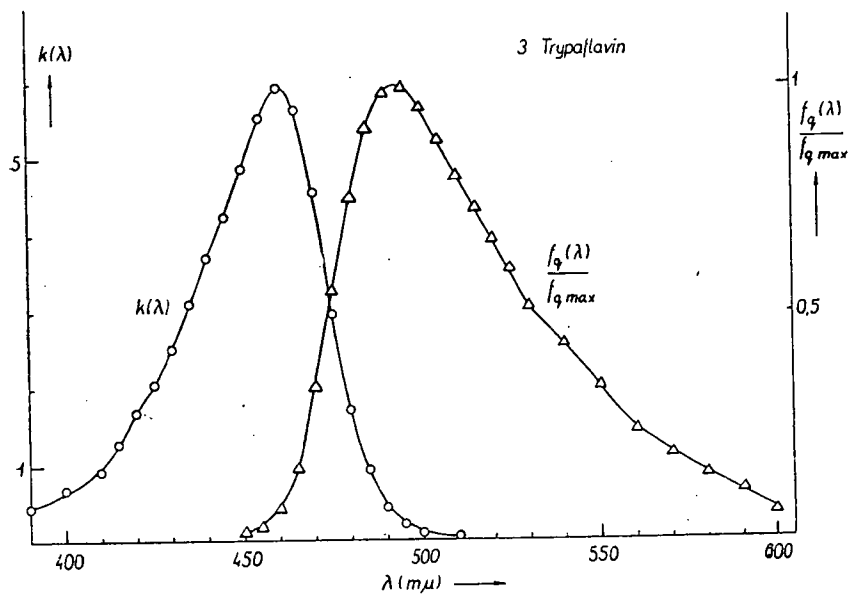


Fig. 3

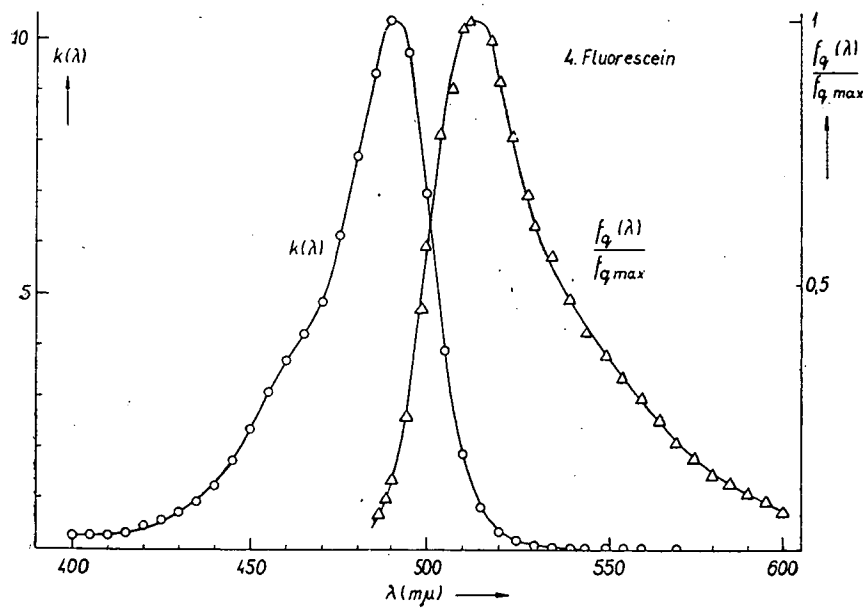


Fig. 4

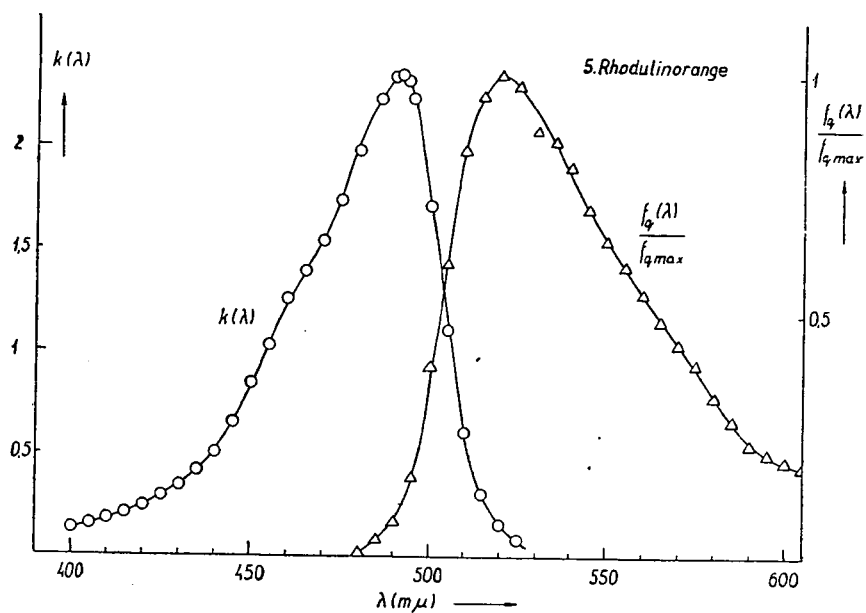


Fig. 5

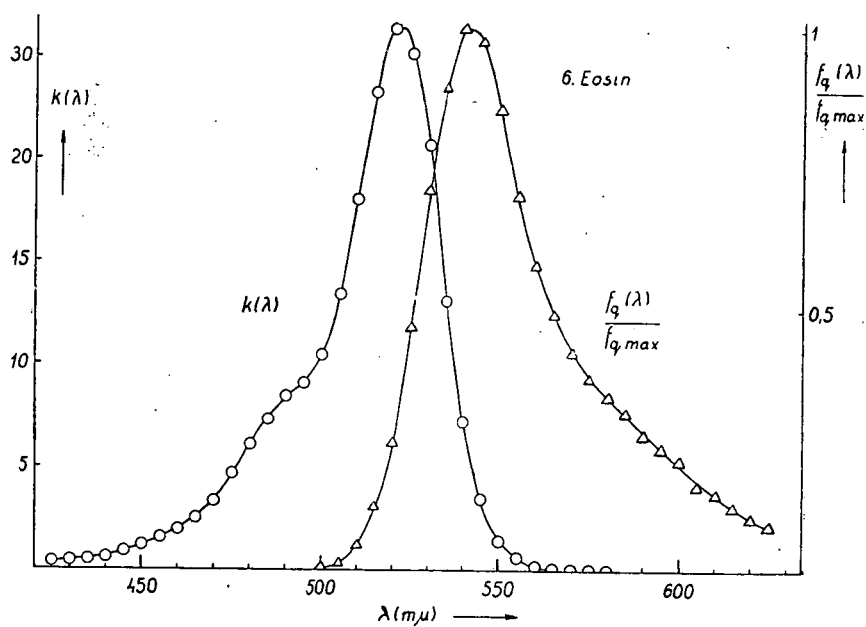


Fig. 6

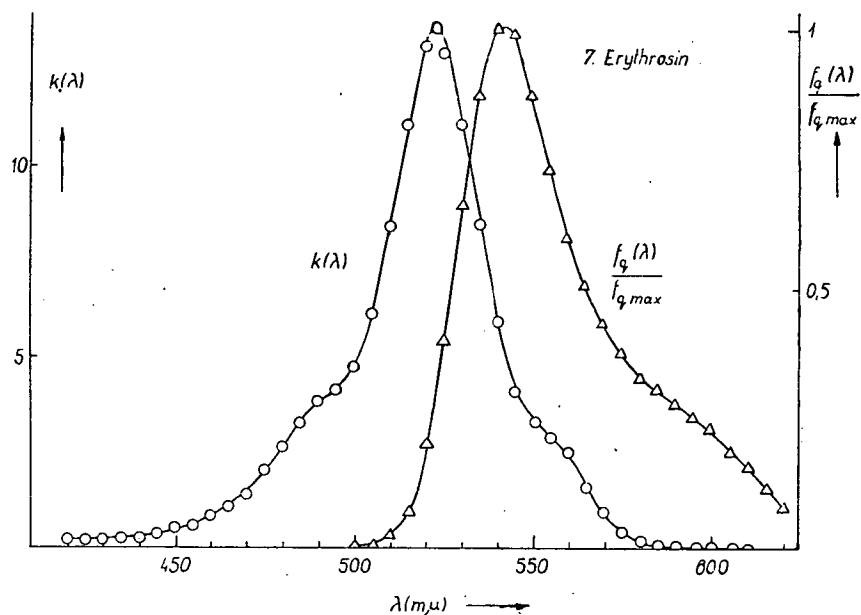


Fig. 7

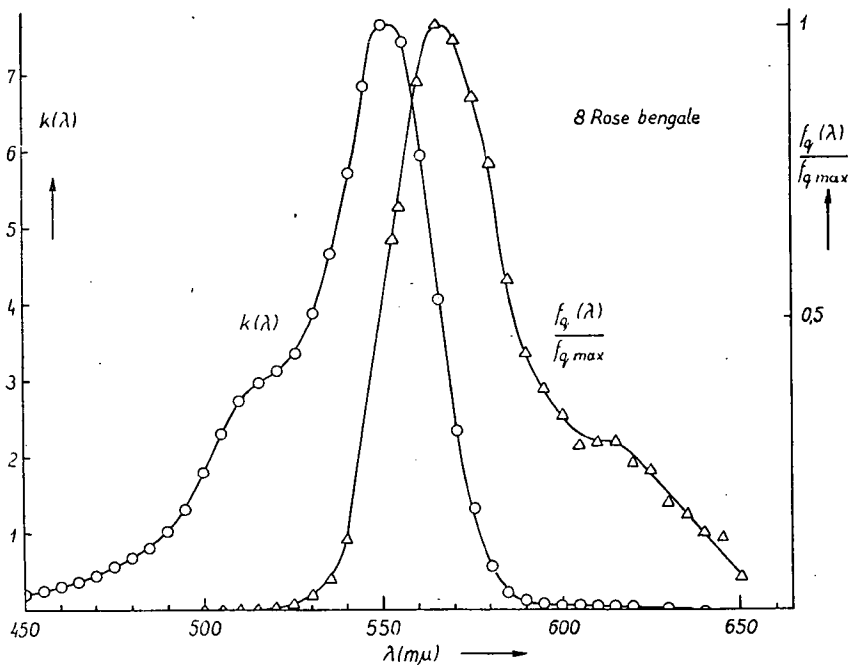


Fig. 8

die so dargestellt sind, daß bei der Maximumstelle λ_1 des Lumineszenzspektrums die Gl. $f_q(\lambda_1) = W_q^T(\lambda_1)$ besteht.¹

Auf Grund der Diagramme der Fig. 11 und der Ergebnisse früherer, in unserem Institute durchgeführter ähnlicher Untersuchungen sind folgende qualitative Gesetzmäßigkeiten bezüglich des Zusammenhanges der Spektren der Lumineszenz- bzw. Temperaturstrahlung festzustellen.² Bei je höheren Wellenlängen das Maximum des Lumineszenzspektrums liegt, um so besser ist die Übereinstimmung zwischen

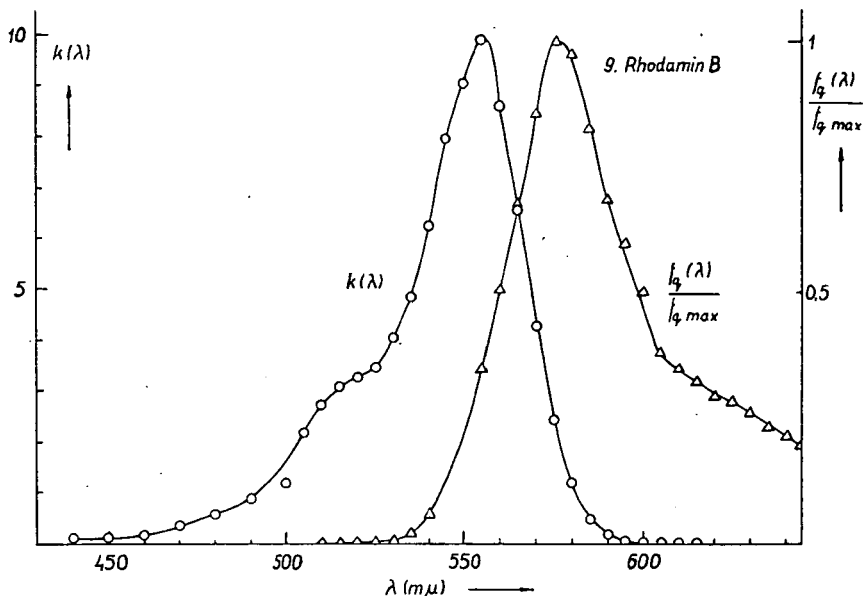


Fig. 9

dem Verlaufe der Funktionen $f_q(\lambda)$ und $W_q^T(\lambda)$. Das bedeutet, der Gl. (5) entsprechend, daß die Funktion $\eta(\lambda)$ bei den blau fluoreszierenden Stoffen bereits in einem dem kurzwelligen Teile des Lumineszenzspektrums entsprechenden Spektralgebiet, bei den orangegelb fluoreszierenden dagegen erst bei größeren Wellenlängen abzufallen beginnt. Im Falle von Eosin und Rose Bengale ergab sich, daß die Funktion $W_q^T(\lambda)$ gegen das Lumineszenzspektrum $f_q(\lambda)$ langwellig verschoben erscheint, dagegen ist der Verlauf der verhältnismäßig hohen T^* -Werten entsprechenden Funktion $W_q^{T*}(\lambda)$ mit demjenigen des Lumineszenzspektrums identisch.

Diese Erfahrungen, in Verbindung mit den früheren [2], [3], weisen darauf hin, daß nicht Gl. (1) bzw. (4), sondern der Zusammenhang (5) im Falle der lumines-

¹ Definitionsgemäß ist $W_q^T(\lambda)d\lambda \equiv \frac{W_e^T(\nu)d\nu}{h\nu}$; $\lambda = \frac{c}{\nu}$; $d\lambda \cong d\nu$.

² Aus den zur Vermeidung der Überfüllung der Figur weggelassenen Spektren des Al-Morins und Rhodulinorange ergibt sich dasselbe, wie im Falle des Äsculins und Fluoreszeins.

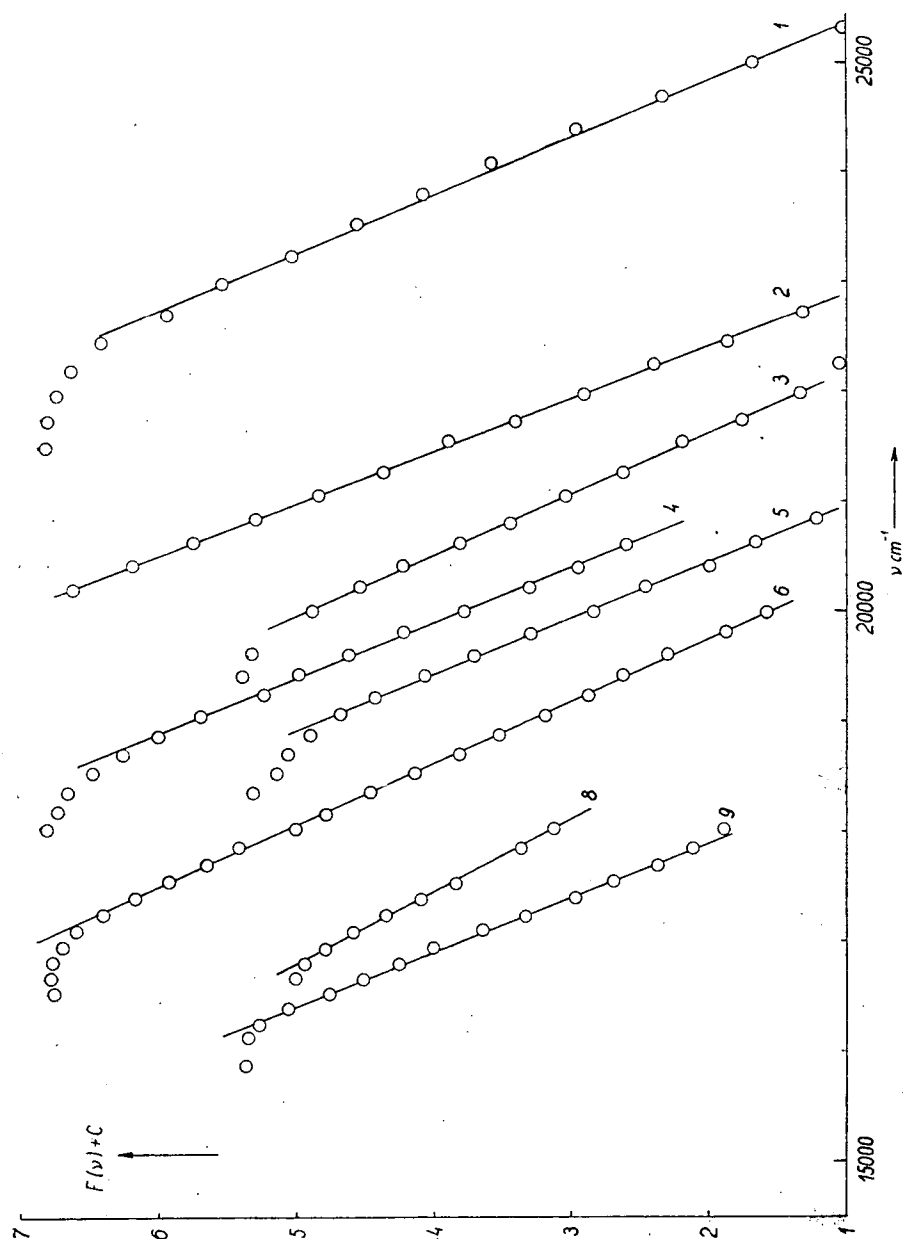


Fig. 10

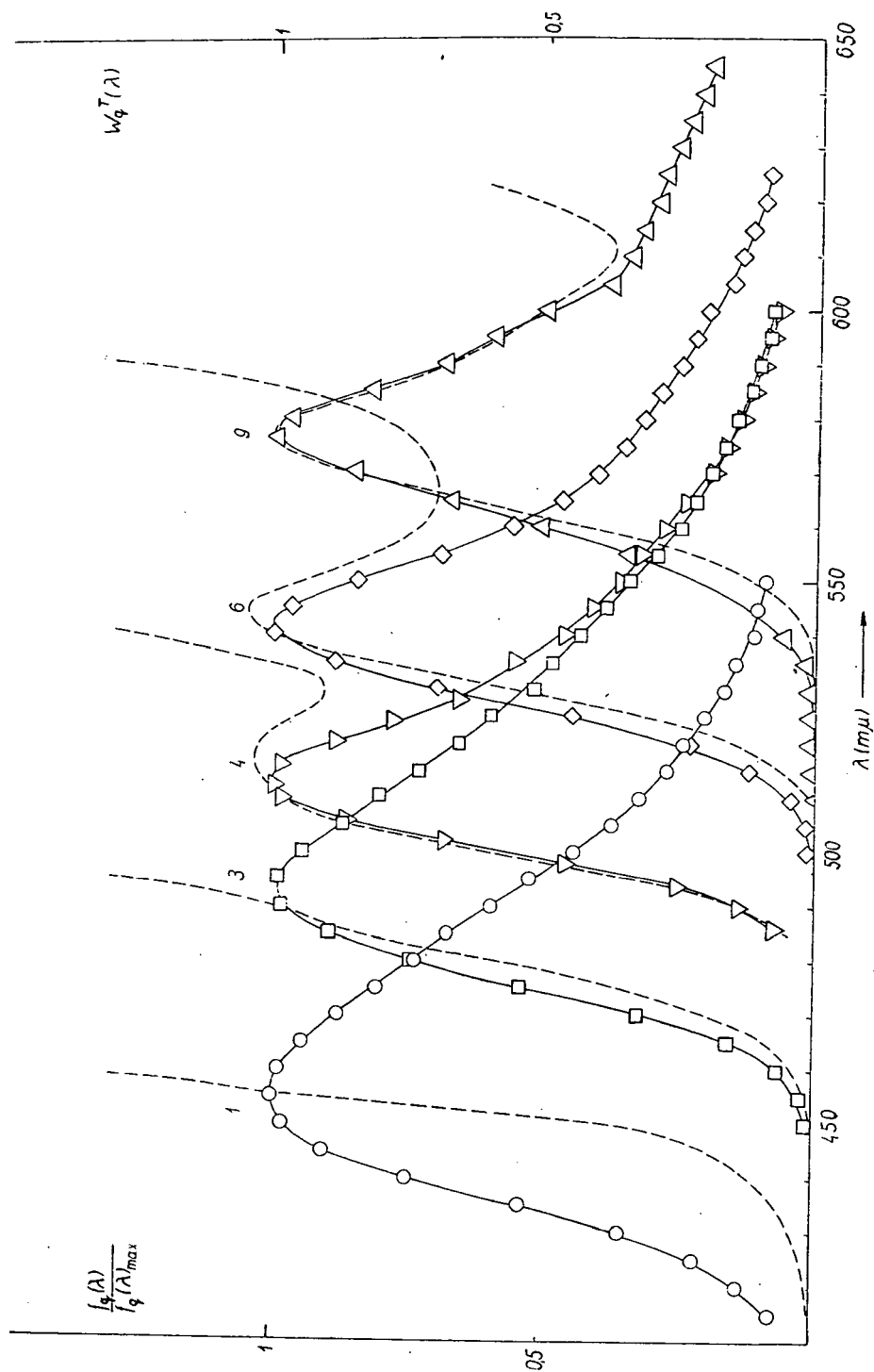


Fig. 11

zierenden Lösungen als eine allgemeinere Gültigkeit besitzende anzusehen ist. Zur Kontrolle des letztgenannten Zusammenhanges sind weitere Versuche im Gange.

* * *

Herrn Prof. Dr. A. BUDÓ, dem Direktor unseres Institutes, spreche ich für seine wertvollen Ratschläge auch hier meinen besten Dank aus.

ЭХПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ ДЛЯ СВЯЗИ ЗАКОНОМЕРНОСТИ ФЛУОРЕСЦЕНТНОГО И ТЕПЛОВОГО ИЗЛУЧЕНИЯ

Л. Козма

Экспериментально исследовалось соотношение Степанова. Данные измерения показывают, что распределение теплового и люминесцентного спектров в случае растворов отличаются.

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NOTE ON THE ACTIVE SPHERE OF LUMINESCENCE QUENCHING

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(Received April 20, 1963)

In the paper [1] HEVESI has published his results about the fluorescence quenching of fluorescein in viscous solution with increase of concentration of the quenching molecules (KI). It was shown that, also in liquid media, the active sphere in JABŁOŃSKI's formula [2] describing the photoluminescence quenching by foreign substances depends on the diffusion coefficient D of the luminescent and quenching molecules.

The simple JABŁOŃSKI's formula for configurational quenching was first applied to the liquid solution in [3]. It was shown that in comparison with rigid solution, the active sphere in liquid solution is greater. The various values of the active sphere for liquid and rigid solutions indicate that it is necessary to introduce in liquid a "collision quenching" in addition to the configuration quenching.

According to HEVESI [1] the value of the active sphere a consists of two parts: one, independent of diffusion, being an effective sphere of configurational quenching and a spherical shell of radius $\sqrt{D\tau}$ around the effective sphere which is to be ascribed to diffusion. Therefore

$$a = A + B\sqrt{D\tau}, \quad (1)$$

where τ is the mean life-time of the excited state of the luminescent molecule for a given concentration of quencher. Only for small concentration of quencher can we suppose that $\tau \approx \tau_0$ (τ_0 mean life-time of luminescent molecule in the absence of quenching molecules).

Author of the present paper obtained another expression for the value of the active sphere of photoluminescence quenching of viscous solutions. According to the theory of diffusion it may be obtained the following formula

$$a = v + 4\pi DR\tau_0, \quad (2)$$

where R denotes the sum of the kinetic radii of the luminescent and quenching. If $D=0$ (rigid solution), $a=v$ and we have only a configurational quenching.

For very small concentration of quenchers the JABŁOŃSKI's formula

$$\frac{\eta}{\eta_0} = \frac{1 - e^{-an}}{en} \quad (3)$$

gives expression

$$\frac{\eta_0}{\eta} = 1 + \frac{1}{2}vn + 2\pi DR\tau_0n \quad (4)$$

identical with the well-known VAVILOV—FRANK relationship for viscous, quenched solution [4].

Fig. 1 shows that the experimental results of HEVESI [1] fit also very good with (2).

The detailed results of our investigations of the above problem will be published later.

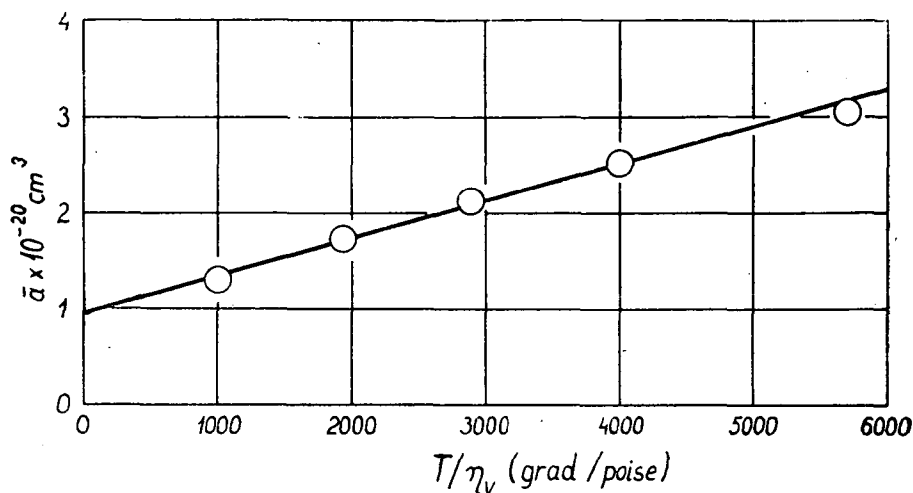


Fig. 1

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UNTERSUCHUNG DER Fe(III)-KOMPLEXE AROMATISCHER SCHIFF-BASEN. IV Resazetophenon-Reihe

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(Eingegangen am 15. Juni 1963.)

Es wurden die Fe(III)-Komplexe der aus Resazetophenon mit aromatischen Aminen gebildeten Schiff-Base untersucht. Es werden zehn verschiedene Fe(III)-Komplexe mit Ihren analytischen Daten und Schmelzpunkten angeführt und besprochen. Die in Alkohol-, Pyridin- und Dimethylsulfoxyd-Lösungen zwischen 200 und 1200 m μ ausgemessenen Spektren weisen eine Struktur auf, die auf kovalente Bindung schließen läßt. Die Banden der für Übergangsmetallionen charakteristischen d-d Übergänge sind aber nicht mit voller Deutlichkeit nachzuweisen. Die Komplexe sind gegen Basen empfindlich; ihre Absorptionskurven zeigen in basischem Medium einen vom in Alkohol ausgemessenen Spektrum bzw. demjenigen der freien Aldehydkomponente vollkommen abweichenden Verlauf. Um 330 m μ erscheinen deutliche Banden von hoher Intensität. Die Verbindungen sind gegen Säuren nicht empfindlich, sie werden zwar gelöst, doch zerfallen sie nicht in ihre Komponenten. Die in solchen Lösungen ausgemessenen Spektren sind denjenigen der Alkoholösungen der betreffenden Komplexe ähnlich.

Mit der Lichtabsorption der Fe(III)-Komplexe von aromatischen Schiff-Basen befaßten wir uns bereits in mehreren [1, 2, 3] Arbeite. Die gegenwärtige Publikation behandelt die Versuchsergebnisse von zehn mit einer weiteren Ligandgruppe gebildeten Komplexen und liefert fernere Daten zur Lösung des Problems.

Versuchsteil

Die Verbindungen der untersuchten Serie wurden in der früher beschriebenen [1, 2] Weise dargestellt. Die Reinigung erfolgte durch Fällung aus Lösungsmitteln bzw. mehrmalige Umkristallisierung. Der Resazetophenon-Aminoäthanol-Komplex war in den von uns angewandten Lösungsmitteln sehr schwer löslich. Die analytischen Daten der Komplexe (C%, H%, N% und Fe%) und ihre Schmelzpunktwerte sind in Tabelle I zusammengefaßt.

Die Absorptionsspektren wurden mittels eines Beckmann DU-Spektrophotometers bei Zimmertemperatur, mit 10, 1,0 und 0,1 cm Quarzküvetten ausgemessen. Die Lösungsmittel wurden mit der in der Literatur allgemein bekannten Methode [4] gereinigt. Die Absorptionskurven und die charakteristischen m μ - und log ϵ Werte sind in den Figuren 3 bis 12 dargestellt, bzw. in den Tabellen II und III zusammengefaßt.

Diskussion der Versuchsergebnisse

Die analytischen Daten des Resazetophenon-Fe(III)Cl-Komplexes, (Tab. I.) liessen auf eine Struktur (Fig. 1) schließen, in der mit der Bildung eines komplexen Kations zu rechnen wäre. Diese Struktur kann aber nicht bestehen, denn auf Einwirkung eines elektrischen Stromes bewegt sich der Komplex weder auf die eine,

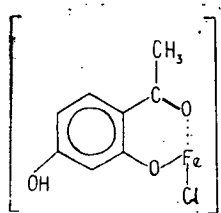


Fig. 1

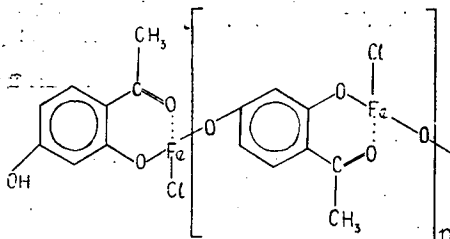


Fig. 2

noch auf die andere Elektrode zu. Er sollte stark paramagnetisch sein, doch entspricht das magnetische Moment (1,13 BM) einem ungepaarten Elektron. Die analytischen Daten des Chlorids (Ber.: 14,63%, Gef.: 14,50) sprechen ebenfalls gegen das Vorhandensein des komplexen Kations. Die im Resazetophenonmolekül in Para-Lage befindliche Hydroxyd des Phenolrings kann ziemlich leicht dissoziieren und dies gibt die Möglichkeit der Verknüpfung von zwei oder mehreren Monomeren (Molekulargewicht 242, 434) zu einem längeren Kettenmolekül (Fig. 2). Die Trimere usw. sind ziemlich schwer löslich.

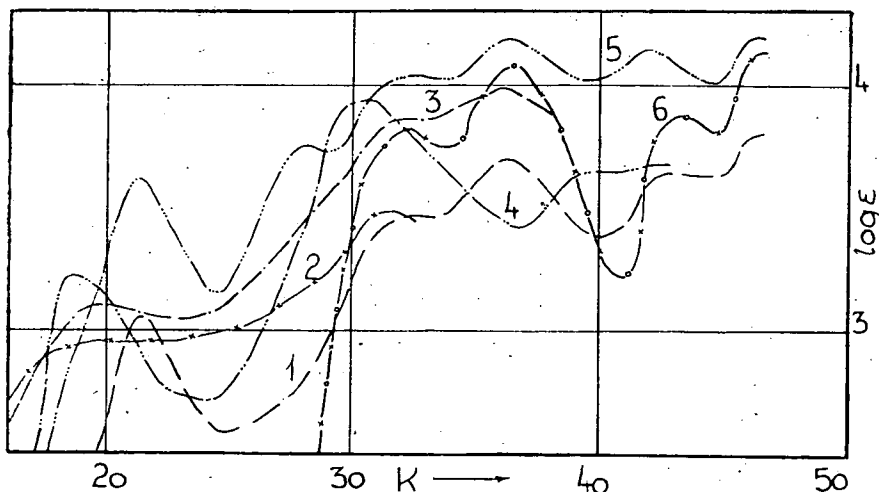


Fig. 3: Resazetophenon-Fe(III) Cl-Komplex (cc=0,000165) Kurve 1: in Äthanol; Kurve 2: in Pyridin; Kurve 3: in DMSO; Kurve 4: in 0,1n NaOH; Kurve 5: in 0,1n HCl; Kurve 6: Resazetophenon in Äthanol.

Die bei der Untersuchung der Struktur der Absorptionskurven feststellbaren, zu den Erregungsprozessen der Liganden gehörigen hohen Banden sind in den in Alkohol ausgemessenen Spektren der Verbindungen größtenteils aufzufinden. Es kann eine geringe Verschiebung nach den langen Wellen beobachtet werden (Fig. 4, 10). Meist ist aber keine wesentliche Änderung festzustellen (Fig. 3, 5–11). Bei einigen Verbindungen (Fig. 3, 4, 12) trat eine Abnahme der Extinktion ein, doch ist die Steigerung der Extinktion für die Gleider der Gruppe charakteristisch (Fig. 5–11). Es kann beobachtet werden, daß die in Alkohol ausgemessenen Spektren der Schiff-Base und des Ketons nahezu gleich sind (Fig. 5–8).

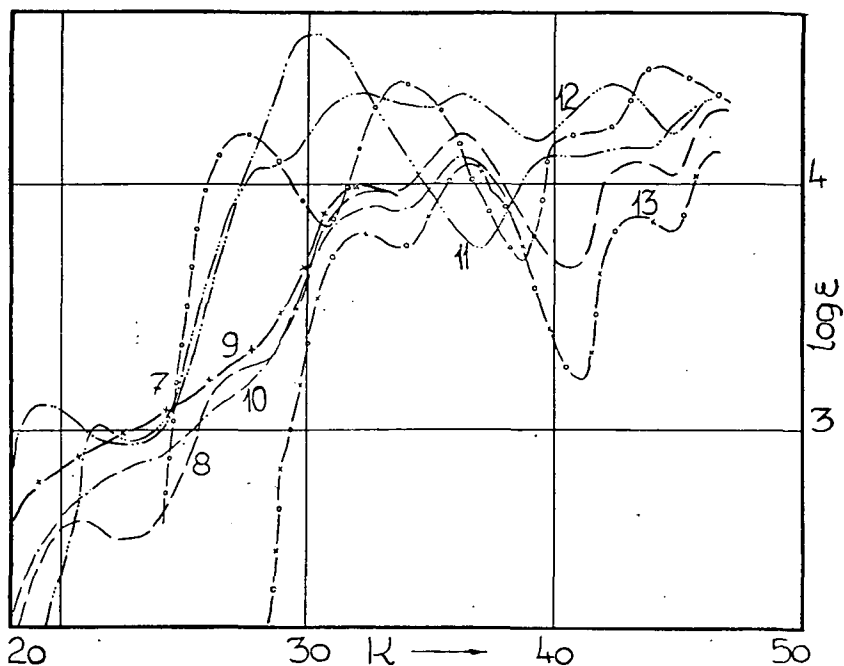


Fig. 4: Kurve 7: Resazetophenon-aminoäthanol in Äthanol; Fe(III) Cl-Komplex ($c = 0,00008339$)
Kurve 8: in Äthanol; Kurve 9: in Pyridin; Kurve 10: in MDSO; Kurve 11: in 0,1n NaOH; Kurve
12: in 0,1n HCl; Kurve 13: Resazetophenon in Äthanol.

Im Vergleich mit den Spektren der Liganden sind die Spektren der Komplexe (Fig. 5, 6, 11) ziemlich verwaschen. In den übrigen Fällen (Fig. 3, 4, 7–10, 12) sind scharfe Banden zu finden. Bei dem Resazetophenon- α -naphthylamin-Komplex befindet sich auch über 500 m μ eine verwaschene Bande mittlerer Intensität.

Bei den in Pyridin ausgemessenen Spektren wurde eine wesentliche Änderung nur im Spektrum des Resazetophenon-o-phenylendiimin-Komplexes (Fig. 12) gefunden, wo eine Bandenverschiebung um 30 m μ nach den kürzeren Wellen erschien. Bei der Verbindung 3 trat eine Intensitätsverminderung ein. In den in Pyridin ausgemessenen Spektren erscheinen — die Verbindung 10 ausgenommen — wohl definierte Banden bei 330–310 m μ .

Die Spektren der Komplexe wurden auch in Dimethylsulföxyd (DMSO) ausgemessen. Die Spektren der Pyridin- und der DMSO-Lösungen sind nur in einem Falle (Fig. 3) ähnlich, die Intensität ist aber in der letzteren Lösung weit höher. Bei den anderen Komplexen ist im Vergleich mit den in Alkohol ausgemessenen Spektren keine wesentliche Änderung zu finden. Eine geringe Extinktionssteigerung ergab sich bloß in drei Fällen (Fig. 8, 9, 11).

Tabelle I

| No | Komplex | C % | | H % | | N % | | Fe % | | Schmelzpunkt. |
|-----|--|-------|----------------|------|--------------|------|--------------|-------|----------------|---------------|
| | | Ber. | Gef. | Ber. | Gef. | Ber. | Gef. | Ber. | Gef. | |
| 1. | Resazetophenon-Fe(III)Cl | 39,65 | 39,77 39,70 | 2,91 | 2,98 3,02 | — | — | 23,04 | 23,00 23,10 | > 350 C° |
| 2. | Resazetophenon-aminoethanol-Fe(III)Cl | 50,00 | 50,10 50,02 | 5,04 | 5,10 5,06 | 5,84 | 5,80 5,91 | 11,64 | 11,70 11,81 | > 350 C° |
| 3. | Resazetophenon-m-aminophenol-Fe(III)Cl | 58,40 | 58,45 58,40 | 4,20 | 4,30 4,25 | 4,86 | 4,70 4,65 | 9,69 | 9,60 9,71 | > 350 C° |
| 4. | Resazetophenon-p-aminophenol-Fe(III)Cl | 58,40 | 58,35 58,49 | 4,20 | 4,16 4,10 | 4,86 | 4,72 4,80 | 9,69 | 9,60 9,65 | 120 C° |
| 5. | Resazetophenon-m-toluidin-Fe(III)Cl | 63,00 | 63,10 63,15 | 4,93 | 4,90 4,93 | 4,90 | 5,01 4,95 | 9,76 | 9,74 9,70 | 101 C° |
| 6. | Resazetophenon-p-toluidin-Fe(III)Cl | 63,00 | 62,94 62,90 | 4,93 | 5,00 5,01 | 4,90 | 4,78 4,85 | 9,76 | 9,80 9,77 | 110 C° |
| 7. | Resazetophenon-p-anisidin-Fe(III)Cl | 59,94 | 59,75 59,80 | 4,64 | 4,60 4,68 | 4,64 | 4,60 4,56 | 9,25 | 9,30 9,26 | 102 C° |
| 8. | Resazetophenon- α -naphthylamin-Fe(III)Cl | 67,15 | 67,20 67,27 | 4,38 | 4,40 4,43 | 4,35 | 4,40 4,38 | 8,67 | 8,70 8,75 | 110 C° |
| 9. | Resazetophenon- β -naphthylamin-Fe(III)Cl | 67,15 | 67,30 67,25 | 4,38 | 4,40 4,36 | 4,35 | 4,46 4,44 | 8,67 | 8,80 8,76 | 97 C° |
| 10. | Resazetophenon-o-phenylendiimin-Fe(III)Cl | 56,73 | 56,74 56,80 | 3,89 | 3,79 3,84 | 6,01 | 6,06 6,02 | 11,98 | 12,01 12,05 | 128 C° |

Bei den in basischen Medium (0,1 n NaOH) ausgemessenen Spektren ist als interessant zu erwähnen, daß um 330 m μ deutliche Banden von hoher Intensität erscheinen. Außerdem sind wesentliche Veränderungen gegen die in Alkohol ausgemessenen Spektren zu beobachten. In der Base fallen die Banden um 276 m μ vollkommen weg.

In saurem Medium (0,1 HCl) sind die Spektren den in Alkohol ausgemessenen vollkommen ähnlich (Fig. 5—9, 11, 12). Eine langwellige Verschiebung konnte im Falle des Resazetophenen-m-toluidin-Komplexes beobachtet werden. In saurer

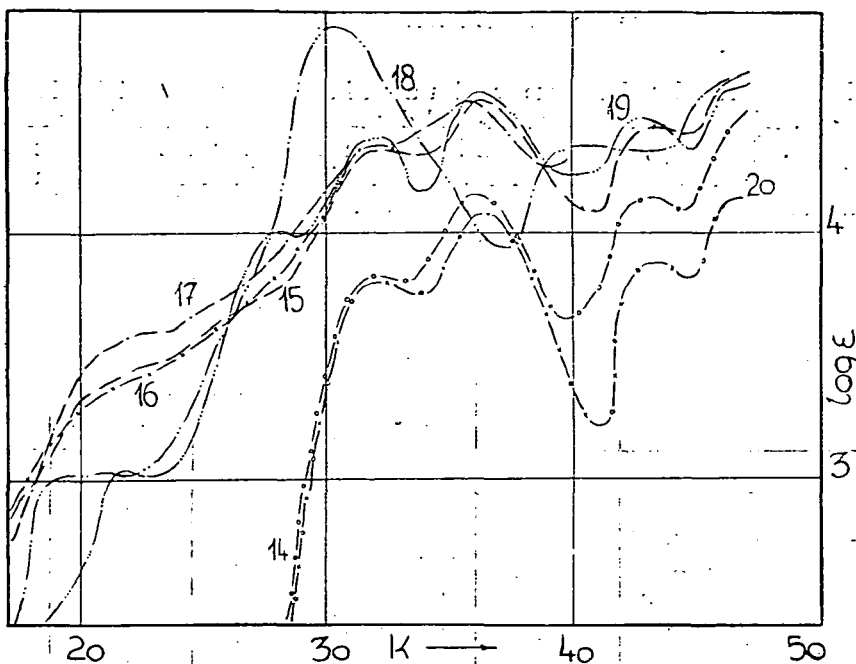


Fig. 5: Kurve 14: Resazetophenon-m-aminophenol in Äthanol; Fe(III)Cl-Komplex ($\epsilon = 0,00006947$)
 Kurve 15: in Äthanol; Kurve 16: in Pyridin; Kurve 17: in DMSO; Kurve 18: in 0,1n NaOH;
 Kurve 19: in 0,1n HCl; Kurve 20: Resazetophenon in Äthanol.

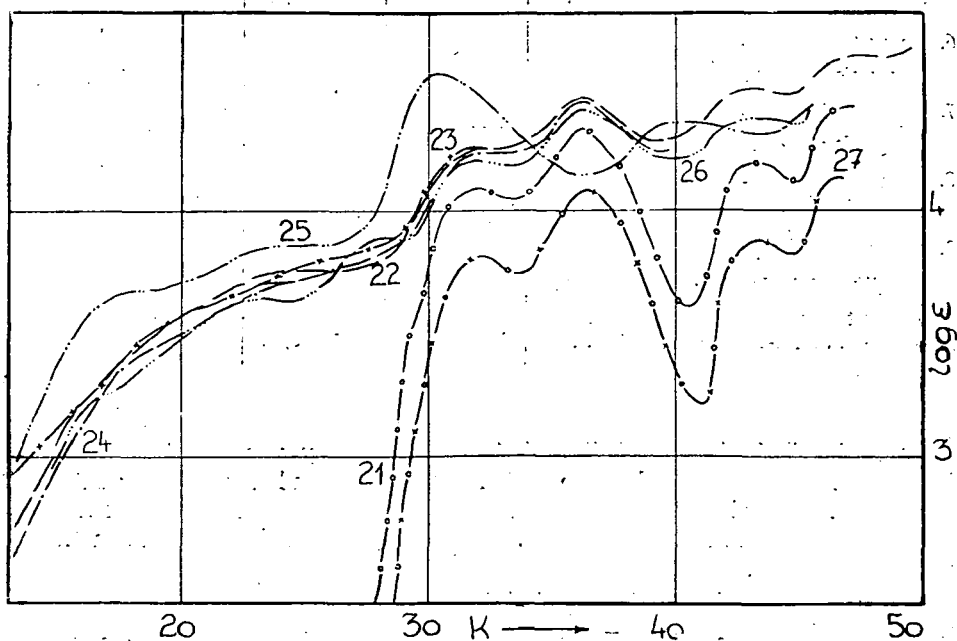


Fig. 6: Kurve 21: Resazetophenon-p-aminophenol in Äthanol; Fe(III)Cl-Komplex ($\epsilon = 0,00006947$)
 Kurve 22: in Äthanol; Kurve 23: in Pyridin; Kurve 24: in DMSO; Kurve 25: in 0,1n NaOH;
 Kurve 26: in 0,1n HCl; Kurve 27: Resazetophenon in Äthanol.

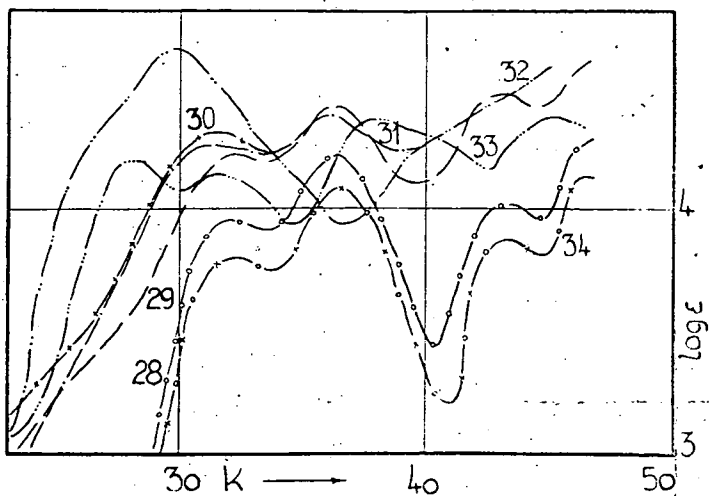


Fig. 7. Kurve 28: Resazetophenon-m-toluidin in Äthanol; Fe(III) Cl-Komplex ($cc=0,0000696$)
 Kurve 29: in Äthanol; Kurve 30: in Pyridin; Kurve 31: in DMSO; Kurve 32: in 0,1n NaOH;
 Kurve 33: in 0,1n HCl; Kurve 34: Resazetophenon in Äthanol.

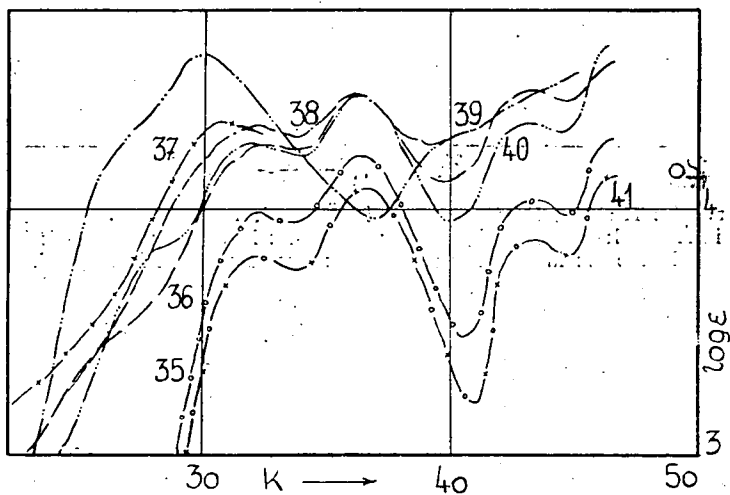


Fig. 8. Kurve 35: Resazetophenon-p-toluidin in Äthanol; Fe(III) Cl-Komplex ($cc=0,00006996$)
 Kurve 36: in Äthanol; Kurve 37: in Pyridin; Kurve 38: in DMSO; Kurve 39: in 0,1n NaOH; Kurve
 40: in 0,1n HCl; Kurve 41: Resazetophenon in Äthanol.

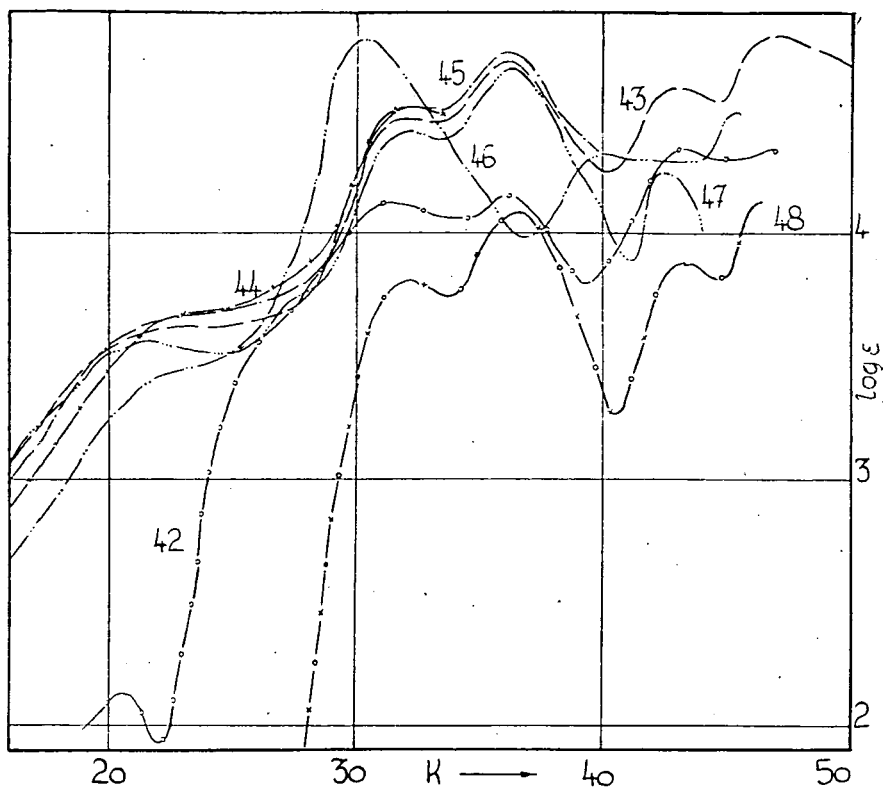


Fig. 9. Kurve 42: Resazetophenon-p-anisidin in Äthanol; Fe(III) Cl-Komplex ($\epsilon = 0,00006625$)
 Kurve 43: in Äthanol; Kurve 44: in Pyridin; Kurve 45: in DMSO; Kurve 46: in 0,1n NaOH;
 Kurve 47: in 0,1n HCl; Kurve 48: Resazetophenon in Äthanol.

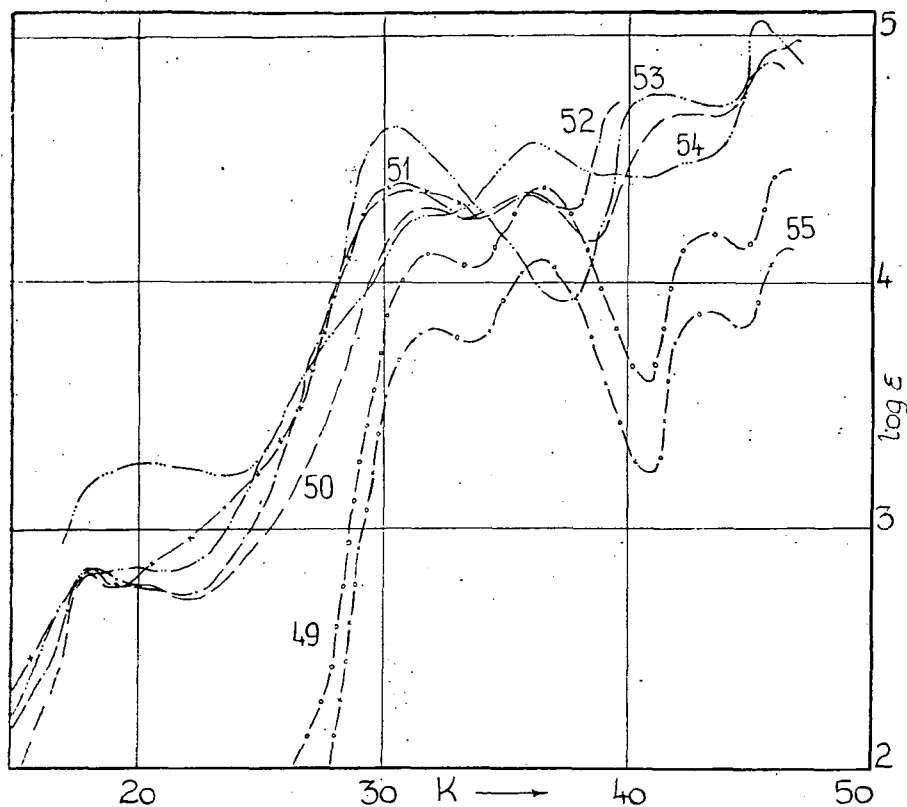


Fig. 10. Kurve 49: Resazetophenon- α -naphthylamin in Äthanol; Fe(III) Cl-Komplex ($c = 0,00006212$)
 Kurve 50: in Äthanol; Kurve 51: in Pyridin; Kurve 52: in DMSO; Kurve 53: in 0,1n NaOH;
 Kurve 54: in 0,1n HCl; Kurve 55: Resazetophenon in Äthanol.

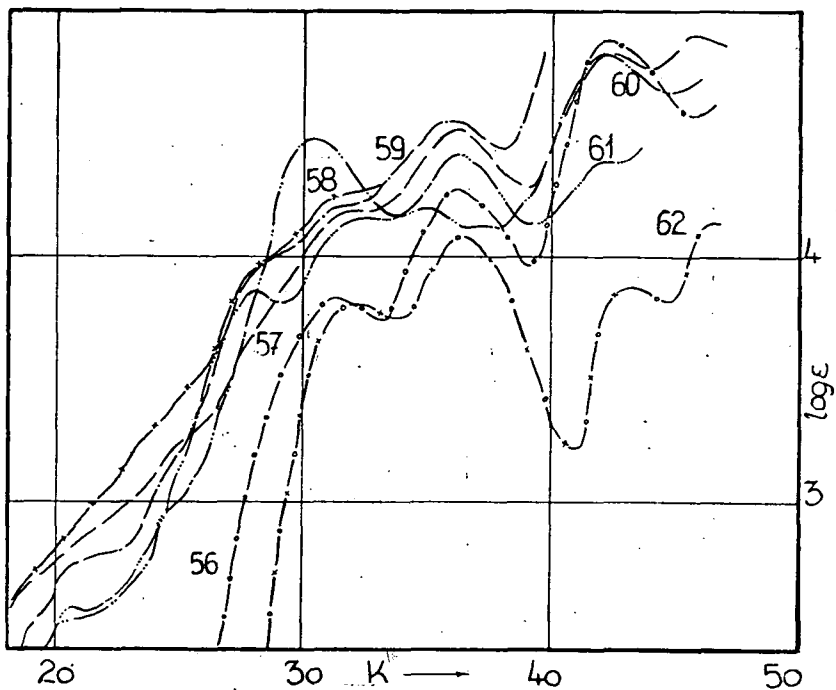


Fig. 11. Kurve 56: Resazetophenon- β -naphthylamin in Äthanol; Fe(III) Cl-Komplex ($c = 0,00006212$)
 Kurve 57: in Äthanol; Kurve 58: in Pyridin; Kurve 59: in DMSO; Kurve 60: in 0,1n NaOH;
 Kurve 61: in 0,1n HCl; Kurve 62: Resazetophenon in Äthanol.

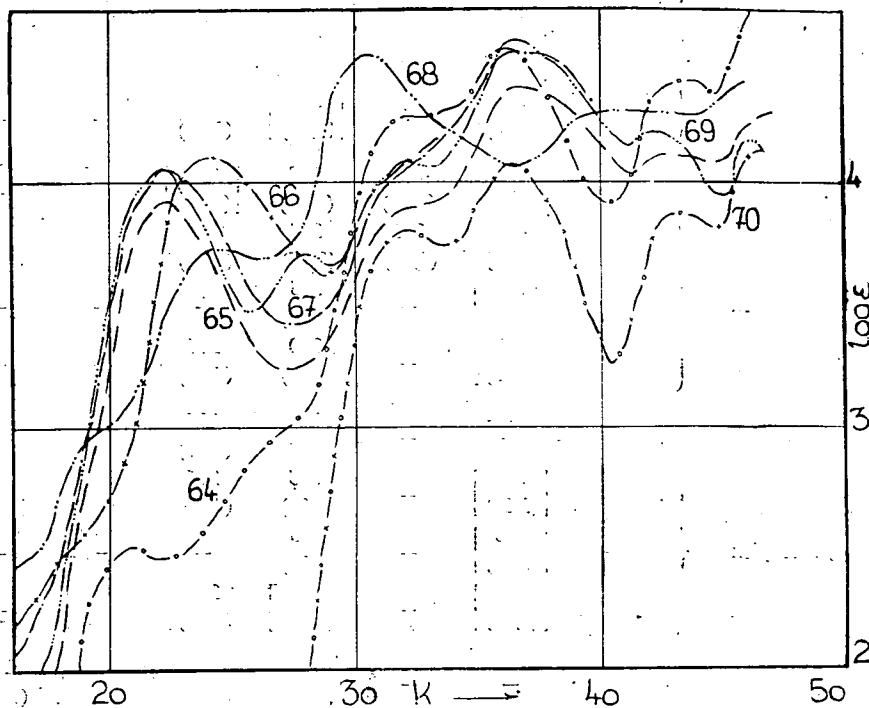


Fig. 12. Kurve 64: Resazetophenon-o-phenylendiimin in Äthanol; Fe(III) Cl-Komplex (cc= 0,00008591) Kurve 65: in Äthanol; Kurve 66: in Pyridin; Kurve 67: in DMSO; Kurve 68: in 0,1n. NaOH; Kurve 69: 0,1n HCl; Kurve 70: Resazetophenon in Äthanol.

Tabelle II

| No | Verbindung | Lösungs- mittel | Banden (mμ und log ε) | | | | | |
|--------------------|--------------------|--------------------|-----------------------|-------------------|-------------------|---------------|-------------------|-------------------|
| 1. Fe(III)-Komplex | Ligand | Alk. | — | — | 315 (3,80) | 276 (4,08) | 232 (3,87) | 216 (4,13) |
| | { | Alk. | 480 (3,06) | — | [310] (3,47) | 276 (3,70) | [232] (3,64) | [218] (3,78) |
| | | Pyridin | [500] (2,95) | — | 320 (3,49) | — | — | — |
| | | DMSO | [500] (3,10) | — | [320] (3,81) | 276 (3,99) | — | — |
| | | 2. Fe(III)-Komplex | Ligand | Alk. | — | 370 (4,21) | 298 (4,42) | [248] (4,19) |
| { | Alk. | | 490 (2,63) | 365 (3,25) | 305 (3,97) | 276 (4,21) | 230 (4,09) | 216 (4,28) |
| | Pyridin | | [500] (2,86) | — | 315 (4,00) | — | — | — |
| | DMSO | | [500] (2,75) | — | 310 (3,91) | 276 (4,06) | — | — |
| | 3. Fe(III)-Komplex | | Ligand | Alk. | — | — | 315 (3,83) | 276 (4,17) |
| { | | Alk. | [500] (3,35) | — | 315 (4,34) | 276 (4,55) | 230 (4,43) | 216 (4,62) |
| | | Pyridin | [500] (3,32) | — | 315 (4,36) | — | — | — |
| | | DMSO | [460] (3,58) | — | [315] (4,34) | 280 (4,53) | — | — |
| | | 4. Fe(II)-Komplex | Ligand | Alk. | — | — | 315 (4,09) | 276 (4,33) |
| { | Alk. | | [500] (3,59) | — | 310 (4,25) | 276 (4,46) | 232 (4,49) | 212 (4,63) |
| | Pyridin | | [500] (3,58) | — | 320 (4,24) | — | — | — |
| | DMSO | | [550] (3,64) | — | 315 (4,23) | 276 (4,44) | — | — |
| | 5. Fe(III)-Komplex | | Ligand | Alk. | — | — | 315 (3,95) | 276 (4,22) |
| { | | Alk. | — | [400] (3,26) | 315 (4,22) | 276 (4,41) | 232 (4,46) | — |
| | | Pyridin | — | — | 320 (4,32) | — | — | — |
| | | DMSO | — | — | 345 (4,26) | 276 (4,38) | — | — |

Tabelle II

| No | Verbindung | Lösungs- mittel | Banden (mμ und log ε) | | | | | |
|---------------------|------------|--------------------|-----------------------|-------------------|-------------------|---------------|---------------|---------------|
| 6. Fe(III)-Komplex | Ligand | Alk. | — | — | 310 (3,98) | 276 (4,22) | 232 (4,03) | 216 (4,27) |
| | { | Alk. | — | [395] (3,41) | 310 (4,26) | 276 (4,45) | 232 (4,48) | — |
| | | Pyridin | — | — | 330 (4,35) | — | — | — |
| | | DMSO | — | — | 315 (4,34) | 276 (4,46) | — | — |
| 7. Fe(III)-Komplex | Ligand | Alk. | 500 (2,13) | [380] (3,61) | 320 (4,12) | 276 (4,15) | 232 (4,34) | 214 (4,33) |
| | { | Alk. | [500] (3,55) | — | 315 (4,46) | 276 (4,70) | 232 (4,59) | 212 (4,80) |
| | | Pyridin | [460] (3,64) | — | 310 (4,52) | — | — | — |
| | | DMSO | [500] (3,56) | — | 310 (4,51) | 276 (4,73) | — | — |
| 8. Fe(III)-Komplex | Ligand | Alk. | — | — | 315 (4,11) | 276 (4,39) | 230 (4,20) | 216 (4,45) |
| | { | Alk. | 560 (2,80) | — | 315 (4,30) | 276 (4,36) | 230 (4,69) | 218 (4,09) |
| | | Pyridin | 560 (2,82) | — | 330 (4,41) | — | — | — |
| | | DMSO | 560 (2,83) | — | 320 (4,37) | 280 (4,35) | — | — |
| 9. Fe(III)-Komplex | Ligand | Alk. | — | — | 320 (3,83) | 276 (4,27) | 236 (4,88) | — |
| | { | Alk. | — | — | 310 (4,18) | 276 (4,51) | 236 (4,82) | 220 (4,91) |
| | | Pyridin | — | [360] (3,94) | [325] (4,21) | — | — | — |
| | | DMSO | — | [360] (3,93) | [325] (4,15) | 280 (4,55) | — | — |
| 10. Fe(III)-Komplex | Ligand | Alk. | 480 (2,51) | — | [315] (4,27) | 276 (4,55) | 232 (4,41) | — |
| | { | Alk. | 450 (3,93) | — | [315] (3,89) | 276 (4,39) | 235 (4,11) | — |
| | | Pyridin | — | 420 (4,10) | — | — | — | — |
| | | DMSO | 450 (4,06) | — | [320] (4,00) | 276 (4,53) | — | — |

Tabelle III

| No | Lösungs- mittel | Baden (m μ und log ϵ) | | | | | | |
|-----|--------------------|-------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1. | B | 540 (3,22) | — | — | 330 (3,94) | 256 (3,64) | 236 (3,68) | — |
| | S | — | 470 (3,61) | 360 (3,75) | 310 (4,04) | 276 (4,19) | 238 (4,16) | 216 (4,20) |
| 2. | B | 530 (3,10) | — | — | 335 (4,61) | 256 (4,09) | 235 (4,12) | — |
| | S | — | 470 (3,02) | 355 (4,08) | 315 (4,37) | 276 (4,37) | 336 (4,41) | — |
| 3. | B | 530 (3,04) | — | — | 335 (4,84) | 248 (4,35) | — | 222 (4,54) |
| | S | — | 470 (3,04) | 360 (4,01) | 315 (4,40) | 276 (4,58) | 236 (4,46) | — |
| 4. | B | 600 (3,64) | 430 (3,85) | — | 330 (4,55) | 248 (4,36) | — | — |
| | S | 600 (3,27) | 440 (3,64) | 355 (3,89) | 315 (4,20) | 276 (4,42) | 230 (4,37) | — |
| 5. | B | — | — | — | 335 (4,65) | 256 (4,21) | — | — |
| | S | — | 460 (4,20) | — | 320 (4,14) | 252 (4,37) | — | 222 (4,37) |
| 6. | B | — | — | 385 (4,20) | 335 (4,63) | 252 (4,27) | — | — |
| | S | — | — | 360 (3,84) | 315 (4,27) | 276 (4,47) | 232 (4,35) | — |
| 7. | B | — | 470 (3,40) | — | 330 (4,79) | 250 (4,34) | — | 222 (4,47) |
| | S | — | 470 (3,56) | — | 315 (4,41) | 276 (4,67) | 236 (4,25) | — |
| 8. | B | 560 (2,80) | 500 (2,83) | — | 330 (4,64) | 244 (4,77) | — | 220 (4,87) |
| | S | — | 480 (3,26) | — | 315 (4,27) | 276 (4,57) | — | 220 (5,06) |
| 9. | B | — | 490 (2,51) | — | 330 (4,47) | 292 (4,19) | 236 (4,82) | — |
| | S | — | 490 (2,57) | 360 (3,86) | 315 (4,14) | 476 (4,42) | 236 (4,39) | — |
| 10. | B | 540 (2,93) | — | 420 (3,37) | 330 (4,53) | 253 (4,28) | — | — |
| | S | — | 460 (4,05) | 360 (3,71) | 315 (4,08) | 276 (4,58) | 236 (4,21) | 218 (4,17) |

B=0,1n NaOH-Äthanol

S=0,1n HCl-Äthanol

Lösung trat bei drei Verbindungen (Fig. 3, 4, 10) eine Intensitätsverminderung im Vergleich mit den in Alkohol ausgemessenen Spektren auf.

* * *

Dem Leiter des Institutes, Herrn Dozenten Dr. F. MÁRTA bin ich für seine prinzipiellen Ratschläge und die Unterstützung meiner Arbeit zu aufrichtigem Danke verpflichtet.

ИЗУЧЕНИЕ Fe(III)-КОМПЛЕКСОВ АРОМАТИЧЕСКИХ ШИФФ-БАЗ. IV

Серия рессацетофенона,

И. Балог

Шифф-база рессацетофенона с ароматическими аминами была изучена. Десять различных Fe(III) комплексов описаны данными анализа и значениями ϵ . Спектры в спиртовых, пиридиновых и диметилсульфоксидных при 200—1200 $m\mu$ показывают структуру, где ковалентные связи ожидаются. Все таки полоса d—d переходов характеризующие металлические ионы не могут быть показаны с точностью ни в этом случае. Комплексы чувствительны на щелочь и их абсорбционные кривые совсем различны чем у спиртовых или свободных альдегидных компонентов. В спектре полученном в щелочном растворе полоса высокой интенсивности появляются при 330 $m\mu$. Соединения не чувствительны на окислы, они растворяются но не падают на компоненты. Спектр такого раствора подобен на спиртовый спектр комплекса.

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UNTERSUCHUNG DER Fe(III)-KOMPLEXE AROMATISCHER SCHIFF-BASEN. V Resorzylaldehyd-Reihe

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(Eingegangen am 15. Juni 1963.)

Es wurden die Fe(III)-Komplexe der mit aromatischen Aminen gebildeten Schiff-Basen des Resorzylaldehyds untersucht. Es werden weitere zehn verschiedene Fe(III)-Kelat-komplexe mit den entsprechenden analytischen Daten und Schmelzpunktwerten angeführt und besprochen. Die Struktur der in alkoholischen, Pyridin- und DMSO-Lösungen zwischen 200 und 1200 m μ aus gemessenen Spektren läßt auf kovalente Bindung schließen. Die Banden der d-d Übergänge sind aber nicht mit voller Sicherheit nachzuweisen.

Die Komplexe sind gegen Basen und Säuren in verschiedenem Maße empfindlich. Die Amino-äthanol und m-Phenylendiamin enthaltenden Komplexe zerfallen in ihre Bestandteile und ergeben Spektren, die denjenigen des freien Aldehyds ähnlich sind. Die meisten Komplexe bleiben aber unverändert und ergeben eine dem in Alkohol ausgemessenen Spektrum des Komplexes ähnliche Struktur.

In mehreren bereits erschienenen Arbeiten befaßten wir uns mit dem Problem der Lichtabsorption der Fe(III)-Komplexe von aromatischen Schiff-Basen. Es ist ziemlich schwer, die Struktur der bekannten Spektren zu deuten. Um der Lösung des Problems näher zu gelangen, werden in gegenwärtiger Mitteilung die Daten von zehn weiteren Komplexen behandelt.

Versuchsteil

Die Komplexe der Serie wurden in der früher beschriebenen Weise [1, 2, 3] dargestellt, mit dem Unterschied, daß *n*-Propanol als Lösungsmittel gebraucht wurde. Die Ausbeute blieb in allen Fällen unter 50%. Die dargestellten Komplexe wurden aus Methanol wiederholt umkristallisiert. Die analytischen Daten (C%, H%, N% und Fe%) sowie die Schmelzpunktwerte der Verbindungen sind in Tabelle I zusammengefaßt.

Die Absorptionsspektren wurden mit dem in den früheren Arbeiten benützten Instrument und denselben Versuchsbedingungen, bzw. Lösungsmitteln ausgemessen [1]. Die Absorptionskurven bzw. deren charakteristische m μ - und log ϵ -Werte sind in den Figuren 1 bis 10, bzw. in den Tabellen II und III enthalten.

Diskussion der Versuchsergebnisse

Die Untersuchung der Struktur der Absorptionsspektren dieser Komplexe zeigt wiederholt, daß die zu den Erregungsprozessen des Liganden gehörigen hohen Banden auch in dem in alkoholischer Lösung ausgemessenen Spektrum des Komplexes auffindbar sind. In den in alkoholischer Lösung ausgemessenen Spektren der komplexen Verbindungen sind die charakteristischen Banden der freien Resorzylaldehyd-Komponente gut zu erkennen, besonders diejenige bei 280 m μ (Fig. 1, 2, 5, 6, 8), in einigen Fällen ist aber diese Bande verwaschen (4, 7, 10). Bei dieser Wellenlänge tritt eine Intensitätsverminderung im Spektrum des Komplexes (Fig. 1, 3, 7, 9, 10) im Verleisch mit demjenigen des Aldehyds auf. Eine geringe Bandenverschiebung (um 4 m μ) zeigt sich in Richtung der langen Wellen (Fig. 4, 7, 10).

In den in Alkohol aufgenommenen Spektren der Schiff-Basen ist bei 410 m μ eine Bande von verhältnismäßig hoher Intensität zu finden, mit Ausnahme der Verbindungen 1 und 3, wo diese Bande nicht erscheint. In dem Spektrum des Komplexes fehlt diese Bande gänzlich (Fig. 4—6) oder erscheint sie nur mit geringer Intensität. Eine Verminderung der Extinktion war ebensowohl zu beobachten

Tabelle I

| No | Komplex | C % | | H % | | N % | | Fe % | | Schmelzpunkt |
|-----|--|-------|----------------|------|--------------|------|--------------|-------|----------------|--------------|
| | | Ber. | Gef. | Ber. | Gef. | Ber. | Gef. | Ber. | Gef. | |
| 1. | Resorzylaldehyd-Fe(III)Cl | 47,19 | 47,10 47,20 | 2,80 | 2,88 2,85 | — | — | 15,28 | 15,22 15,26 | > 350 C° |
| 2. | Resorzylaldehyd-anilin-Fe(III)Cl | 60,54 | 60,58 60,64 | 3,88 | 3,82 3,86 | 5,43 | 5,24 5,20 | 10,83 | 10,90 10,96 | > 350 C° |
| 3. | Resorzylaldehyd-aminoäthanol-Fe(III)Cl | 47,86 | 47,76 47,80 | 4,43 | 4,35 4,40 | 6,20 | 6,15 6,10 | 12,38 | 12,25 12,34 | > 350 C° |
| 4. | Resorzylaldehyd-m-aminophenol-Fe(III)Cl | 57,05 | 56,95 56,90 | 3,65 | 3,70 3,62 | 5,11 | 5,06 5,08 | 10,20 | 10,02 10,10 | > 350 C° |
| 5. | Resorzylaldehyd-p-aminophenol-Fe(III)Cl | 57,05 | 56,88 56,94 | 3,65 | 3,68 3,75 | 5,11 | 5,15 5,16 | 10,20 | 10,22 10,26 | 210 C° |
| 6. | Resorzylaldehyd-m-toluidin-Fe(III)Cl | 61,84 | 61,88 61,78 | 4,42 | 4,40 4,48 | 5,15 | 5,15 5,10 | 10,78 | 10,86 10,75 | 177 C° |
| 7. | Resorzylaldehyd-p-toluidin-Fe(III)Cl | 61,84 | 61,80 61,90 | 4,42 | 4,50 4,55 | 5,15 | 5,20 5,15 | 10,78 | 10,80 10,78 | 182 C° |
| 8. | Resorzylaldehyd-p-anisidin-Fe(III)Cl | 58,40 | 58,48 58,40 | 4,17 | 4,20 4,27 | 4,78 | 4,84 4,88 | 9,70 | 9,80 9,85 | 170 C° |
| 9. | Resorzylaldehyd-äthylendiimin-Fe(III)Cl | 49,83 | 49,87 49,80 | 3,63 | 3,70 3,75 | 7,27 | 7,30 7,35 | 14,50 | 14,56 14,58 | > 350 C° |
| 10. | Resorzylaldehyd-m-phenylendiimin-Fe(III)Cl | 60,31 | 60,20 60,25 | 4,25 | 4,30 4,35 | 5,41 | 5,48 5,45 | 10,79 | 10,80 10,75 | > 350 C° |

Tabelle II

| No | Verbindung | Lösungs- mittel | Banden ($m\mu$ und $\log \epsilon$) | | | | | | | |
|----|-----------------|--------------------|---------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1. | Fe(III)-Komplex | Ligand | Alk. | — | — | — | [315] (4,00) | 280 (4,32) | 234 (4,10) | 216 (4,27) |
| | | { | Alk. | 480 (3,60) | — | — | 300 (4,03) | — | [240] (4,16) | [216] (4,34) |
| | | | Pyridin | 520 (2,63) | — | — | 310 (3,43) | — | — | — |
| | | | DMSO | 480 (3,54) | — | — | [315] (4,13) | 380 (4,34) | — | — |
| 2. | Fe(III)-Komplex | Ligand | Alk. | — | 410 (3,65) | 340 (4,40) | — | [280] (4,01) | — | [222] (4,31) |
| | | { | Alk. | — | 420 (3,34) | — | 315 (4,13) | 280 (4,35) | 232 (4,41) | 218 (4,44) |
| | | | Pyridin | — | — | 350 (4,30) | — | — | — | — |
| | | | DMSO | 540 (2,83) | [440] (3,33) | 350 (4,34) | [296] (4,22) | 252 (4,26) | — | — |
| 3. | Fe(III)-Komplex | Ligand | Alk. | — | — | 370 (3,90) | 305 (4,25) | [252] (3,91) | [232] (4,15) | — |
| | | { | Alk. | [520] (3,16) | [400] (3,17) | — | [315] (3,76) | 280 (3,90) | [232] (4,12) | — |
| | | | Pyridin | [500] (3,40) | — | — | 310 (3,67) | — | — | — |
| | | | DMSO | [500] (3,40) | — | — | 315 (4,34) | 280 (4,43) | 252 (4,44) | — |
| 4. | Fe(III)-Komplex | Ligand | Alk. | — | 410 (3,73) | 340 (4,36) | — | [284] (4,14) | [232] (4,27) | — |
| | | { | Alk. | — | — | [350] (4,40) | — | 284 (4,47) | — | [218] (4,86) |
| | | | Pyridin | — | — | 350 (4,23) | 305 (4,24) | — | — | — |
| | | | DMSO | — | — | 350 (4,01) | — | 284 (4,02) | — | — |
| 5. | Fe(III)-Komplex | Ligand | Alk. | — | [410] (3,73) | 345 (4,07) | — | 280 (4,04) | [236] (4,03) | [216] (4,20) |
| | | { | Alk. | — | — | [340] (4,04) | [325] (4,17) | 280 (4,41) | [230] (4,39) | [218] (4,53) |
| | | | Pyridin | [520] (3,50) | — | 345 (4,56) | — | — | — | — |
| | | | DMSO | — | [440] (3,27) | 350 (4,21) | — | 284 (4,48) | — | — |

Tabelle II

| No | Verbindung | Lösungs- mittel | Banden (m μ und log ϵ) | | | | | | | |
|-----|-----------------|--------------------|--------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 6. | Fe(III)-Komplex | Ligand | Alk. | — | [410 (3,72)] | 340 (4,34) | — | [284 (4,04)] | [236 (4,29)] | — |
| | | { | Alk. | — | — | — | [315 (4,06)] | 280 (4,36) | 232 (4,29) | — |
| | | | Pyridin | — | — | 340 (4,45) | — | — | — | — |
| | | | DMSO | — | — | 340 (4,49) | — | 288 (4,48) | — | — |
| 7. | Fe(III)-Komplex | Ligand | Alk. | — | [410 (3,94)] | 340 (4,67) | — | [284 (4,27)] | [240 (4,40)] | [224 (4,50)] |
| | | { | Alk. | — | [420 (3,72)] | 340 (4,16) | — | 284 (4,20) | 232 (4,37) | — |
| | | | Pyridin | — | — | 350 (4,53) | — | 292 (4,37) | — | — |
| | | | DMSO | — | — | 345 (4,52) | — | [288 (4,23)] | — | — |
| 8. | Fe(III)-Komplex | Ligand | Alk. | — | [410 (3,76)] | 345 (4,46) | — | [284 (4,08)] | [240 (4,22)] | [222 (4,30)] |
| | | { | Alk. | [500 (3,18)] | [450 (3,32)] | — | [320 (4,10)] | 280 (4,34) | [236 (4,28)] | 220 (4,57) |
| | | | Pyridin | [520 (3,02)] | — | 345 (4,55) | — | — | — | — |
| | | | DMSO | [500 (3,34)] | — | 350 (4,68) | — | [292 (4,54)] | — | — |
| 9. | Fe(III)-Komplex | Ligand | Alk. | — | [365 (3,78)] | 305 (4,34) | 280 (4,36) | [252 (3,93)] | [232 (4,31)] | — |
| | | { | Alk. | — | [400 (3,17)] | — | [316 (3,76)] | 280 (3,90) | 232 (3,82) | — |
| | | | Pyridin | 500 (2,93) | — | — | 310 (3,94) | — | — | — |
| | | | DMSO | — | [400 (3,60)] | — | [315 (4,14)] | 280 (4,19) | — | — |
| 10. | Fe(III)-Komplex | Ligand | Alk. | — | [410 (3,96)] | 340 (4,47) | — | 284 (4,32) | [236 (4,48)] | — |
| | | { | Alk. | [480 (3,76)] | — | — | — | [284 (4,10)] | 236 (4,22) | [214 (4,38)] |
| | | | Pyridin | — | — | [345 (4,02)] | 300 (4,06) | — | — | — |
| | | | DMSO | [480 (3,91)] | — | [360 (4,27)] | — | [292 (4,39)] | 252 (4,47) | — |

Tabelle III

| No | Lösungs- mittel | Banden (m μ und log ϵ) | | | | | | |
|-----|--------------------|--------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1. | B | 490 (2,54) | — | — | 325 (3,60) | [252] (4,38) | [232] (4,54) | — |
| | S | — | 450 (3,75) | [355] (3,89) | [320] (4,16) | 286 (4,39) | [236] (4,53) | [216] (4,65) |
| 2. | B | 520 (2,95) | — | [360] (4,18) | 320 (4,26) | — | [236] (4,49) | — |
| | S | — | — | 360 (4,18) | 310 (4,45) | 280 (4,53) | 236 (4,62) | — |
| 3. | B | 510 (2,88) | — | — | 320 (4,20) | [260] (3,43) | [232] (3,88) | — |
| | S | — | — | [350] (4,26) | 315 (4,43) | — | 236 (4,37) | — |
| 4. | B | — | [430] (3,72) | — | [320] (4,05) | — | 236 (4,40) | — |
| | S | — | — | 360 (4,32) | 320 (4,45) | 280 (4,60) | [232] (4,74) | — |
| 5. | B | 580 (3,42) | 420 (4,38) | [350] (4,27) | 320 (4,28) | — | [236] (4,34) | — |
| | S | — | — | 370 (4,14) | [315] (4,24) | 280 (4,44) | 232 (4,42) | [218] (4,50) |
| 6. | B | — | [400] (3,88) | — | 325 (4,39) | — | 232 (4,44) | — |
| | S | — | — | 360 (4,06) | [310] (4,43) | 280 (4,62) | 236 (4,46) | — |
| 7. | B | 500 (3,23) | — | [360] (4,46) | [325] (4,52) | — | 232 (4,70) | — |
| | S | — | — | — | 315 (4,27) | 280 (4,43) | 232 (4,40) | — |
| 8. | B | — | — | [365] (4,43) | [305] (4,48) | — | 232 (4,60) | — |
| | S | 500 (3,03) | — | 360 (3,75) | [315] (4,15) | — | 232 (4,33) | 218 (4,50) |
| 9. | B | — | — | — | 325 (4,18) | — | [234] (4,28) | — |
| | S | — | — | — | [310] (4,11) | 280 (4,16) | 232 (4,13) | [216] (4,27) |
| 10. | B | — | — | — | 320 (3,99) | — | 240 (3,98) | — |
| | S | — | 450 (3,78) | 360 (3,95) | [315] (4,13) | 280 (4,37) | 236 (4,37) | — |

B=0,1n NaOH-Äthanol

S=0,1n HCl-Äthanol

(Fig. 1, 3, 7, 9, 10) als eine Steigerung (Fig. 4, 5). Bandenverschiebung zeigte sich sowohl in Richtung der längeren (Fig. 4, 9, 10) als auch der kurzen Wellen (Fig. 2, 3, 6–8). In den Spektren der Komplexe erscheinen auch um $500\text{ m}\mu$ Banden von verhältnismäßig hoher Intensität bzw. Inflexionen (Fig. 1, 3, 8, 10), während sie in anderen Fällen fehlen (Fig. 2, 4, 5–7, 9). In den in alkoholischer Lösung ausgemessenen Spektren erscheinen die Banden im allgemeinen verwaschen.

In Pyridinlösungen wird die Extinktion der Banden größtenteils gesteigert (Fig. 5–7, 9, 10), doch ist sie in einigen Fällen vermindert (Fig. 1, 3, 4). In den Spektren sind höchstens zwei Banden bzw. Inflexionen um $500\text{ m}\mu$ und $300\text{ m}\mu$ festzustellen. Im langwelligen Gebiete erfolgt eine Bandenverschiebung um $20\text{ m}\mu$ (Fig. 1, 5, 8), während im Gebiete der kürzeren Wellen nur bei zwei Verbindungen eine erheblichere Bandenverschiebung erscheint (Fig. 4, 9).

Bei den in DMSO-Lösung ausgemessenen Spektren erreicht die Anzahl der Banden fünf (Fig. 2); der Verlauf der Kurven ist ziemlich verwaschen und demjenigen in alkoholischer Lösung ähnlich. Die erscheinenden Banden sind durch eine Extinktionssteigerung charakterisiert, mit Ausnahme eines Komplexes (Fig. 4). Eine verhältnismäßig geringe Bandenverschiebung ist in langwelliger (Fig. 2, 6, 7) bzw. in kurzwelliger Richtung (Fig. 5) zu beobachten. Als interessant ist zu erwähnen, daß bei zwei Komplexen (Fig. 2, 4) auch über $500\text{ m}\mu$ eine Inflexion bzw. Bande erscheint, die in dem Spektrum der alkoholischen Lösung vollkommen fehlt; in diesen Spektren kann im kurzwelligigen Gebiete eine Extinktionsverminderung beobachtet werden.

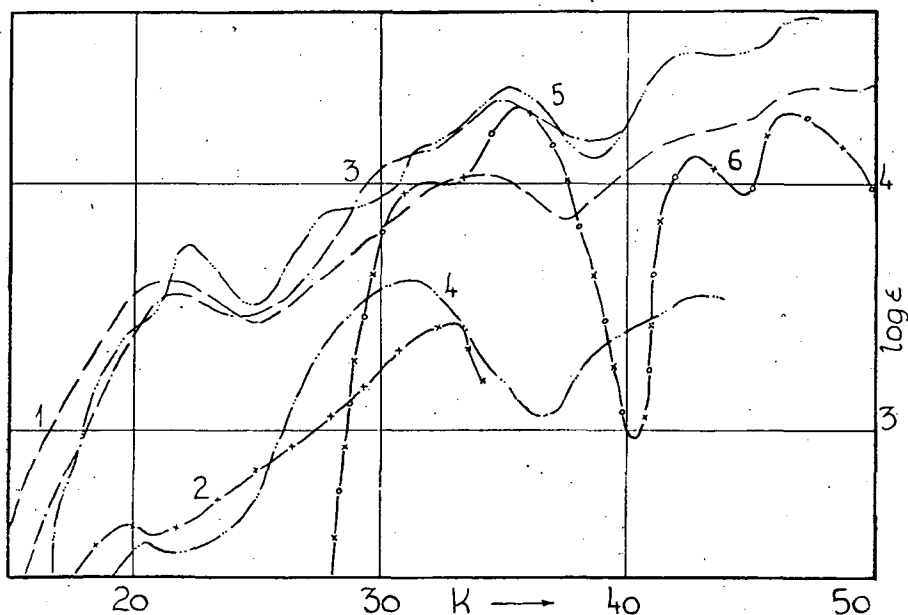


Fig. 1. Resorzylaldehyd-Fe(III) Cl-Komplex ($c = 0,0006087$) Kurve 1: in Äthanol; Kurve 2: in Pyridin; Kurve 3: in DMSO; Kurve 4: in $0,1\text{N NaOH}$; Kurve 5: in $0,1\text{N HCl}$; Kurve 6: Resorzylaldehyd in Äthanol.

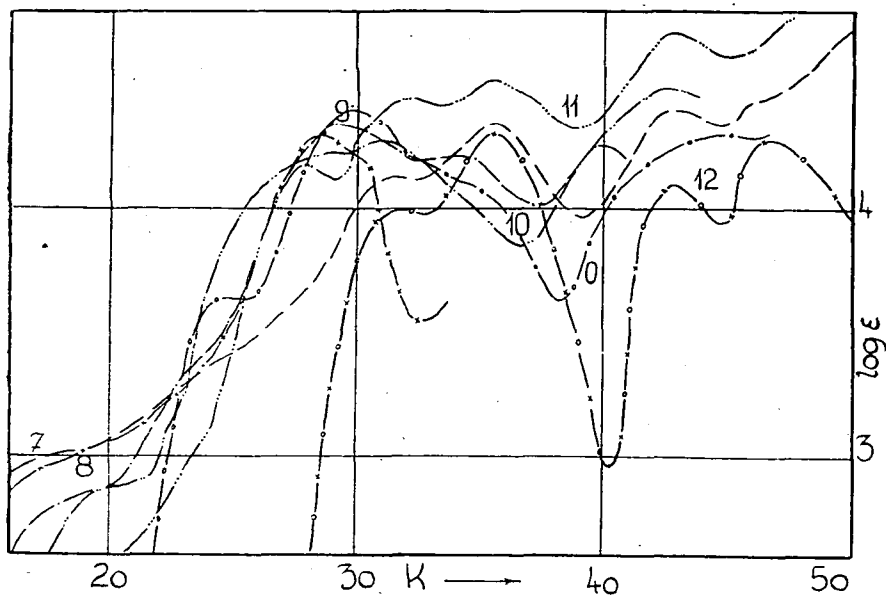


Fig. 2. Kurve 0: Resorzyaldehyd-anilin in Äthanol; Fe(III) Cl-Komplex ($\epsilon = 0.00007758$) Kurve 7: in Äthanol; Kurve 8: in Pyridin; Kurve 9: in DMSO; Kurve 10: in 0,1n NaOH; Kurve 11: in 0,1n HCl; Kurve 12: Resorzyaldehyd in Äthanol.

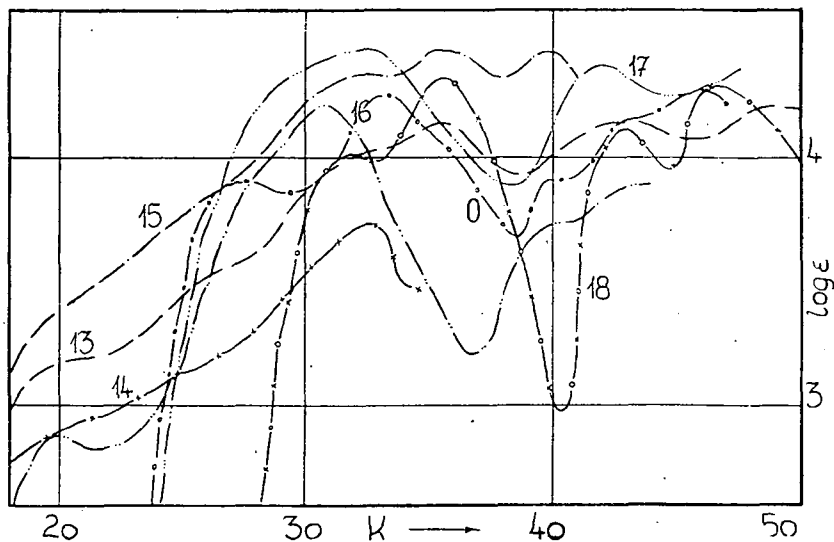


Fig. 3. Kurve 0: Resorzyaldehyd-aminoäthanol in Äthanol; Fe(III) Cl-Komplex ($\epsilon = 0.00009535$) Kurve 13: in Äthanol; Kurve 14: in Pyridin; Kurve 15: in DMSO; Kurve 16: in 0,1n NaOH; Kurve 17: 0,1n HCl; Kurve 18: Resorzyaldehyd in Äthanol.

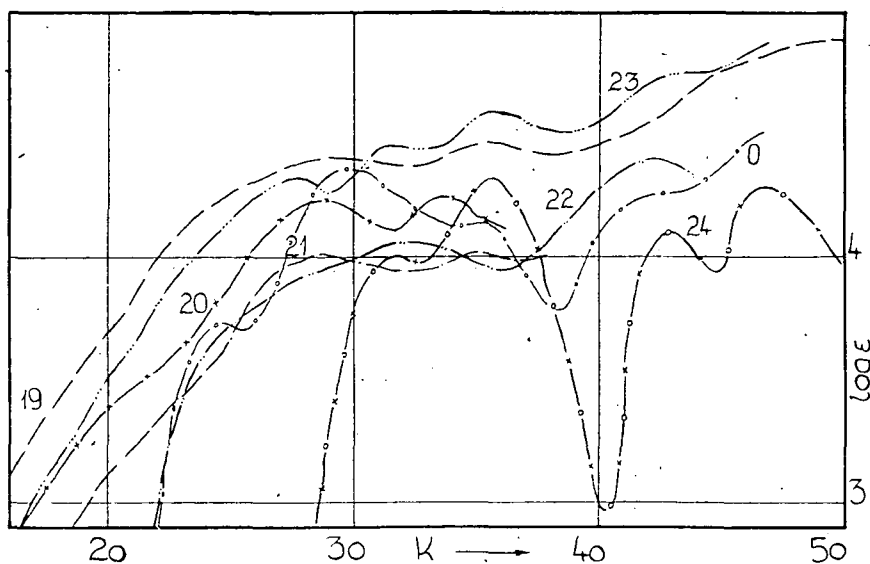


Fig. 4. Kurve 0: Resorzylaldehyd-m-aminophenol in Äthanol; Fe(III) Cl-Komplex ($cc=0,00007275$) Kurve 19: in Äthanol; Kurve 20: in Pyridin; Kurve 21: in DMSO; Kurve 22: in 0,1n NaOH; Kurve 23: in 0,1n HCl; Kurve 24: Resorzylaldehyd in Äthanol.

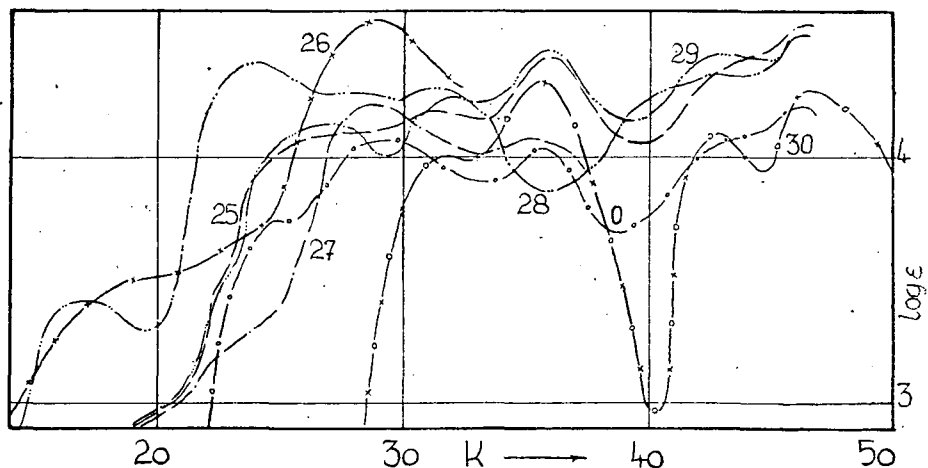


Fig. 5. Kurve 0: Resorzylaldehyd-p-aminophenol in Äthanol; Fe(III) Cl-Komplex ($cc=0,00007305$) Kurve 25: in Äthanol; Kurve 26: in Pyridin; Kurve 27: in DMSO; Kurve 28: in 0,1n NaOH; Kurve 29: in 0,1n HCl; Kurve 30: Resorzylaldehyd in Äthanol.

In alkoholischer Lösung von 0,1 *n* NaOH bzw. 0,1 *n* HCl sind die Komplexe gut lösbar. Im basischen Medium zerfallen die Komplexe 3, 6, 8 und 10, in saurem Medium die Komplexe 3, 7, 9 und 10 in ihre Bestandteile. Ihre Spektren sind denjenigen der freien Aldehydkomponente ähnlich bloß ziemlich stark gegen die län-

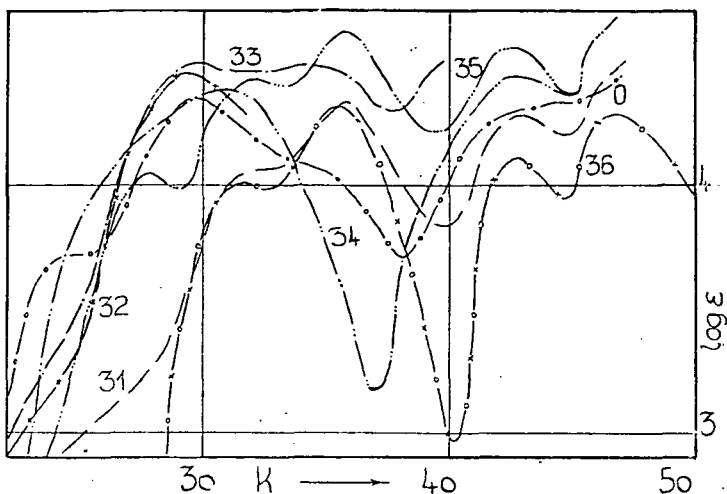


Fig. 6. Kurve 0: Resorzylaldehyd-m-toluidin in Äthanol; Fe(III) Cl-Komplex ($\epsilon = 0,00007342$)
Kurve 31: in Äthanol; Kurve 32: in Pyridin; Kurve 33: in DMSO; Kurve 34: in 0,1n NaOH;
Kurve 35: in 0,1n HCl; Kurve 36: Resorzylaldehyd in Äthanol.

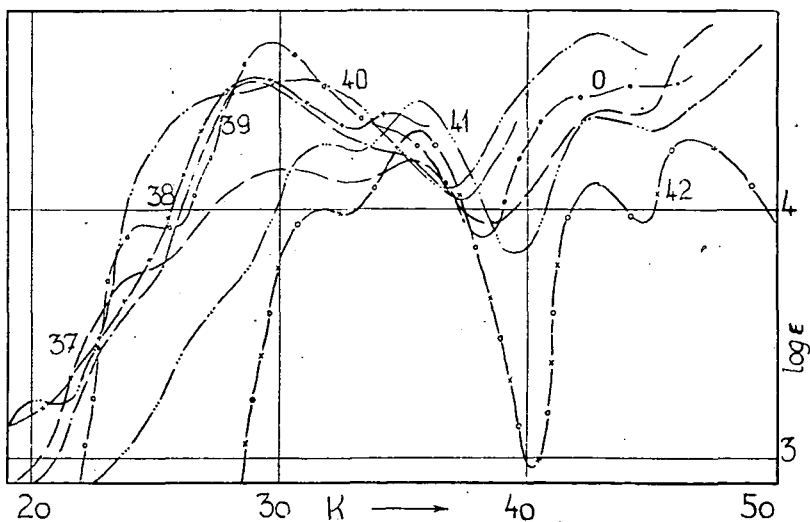


Fig. 7. Kurve 0: Resorzylaldehyd-p-toluidin in Äthanol; Fe(III) Cl-Komplex ($\epsilon = 0,00007342$)
Kurve 37: in Äthanol; Kurve 38: in Pyridin; Kurve 39: in DMSO; Kurve 40: in 0,1n NaOH;
Kurve 41: in 0,1n HCl; Kurve 42: Resorzylaldehyd in Äthanol.

geren Wellen verschoben (Fig. 6, 8). Die übrigen Komplexe ergeben sowohl im basischen (Fig. 1, 4, 5), als auch im sauren Medium (Fig. 1, 2, 4, 6, 8) Kurven, deren Verlauf demjenigen des Spektrums in alkoholischer Lösung ähnlich ist. Eine Extinktionssteigerung ist sowohl bei den Banden der in basischer (Fig. 2, 5–9) als denjenigen der in saurer Lösung ausgemessenen Spektren (Fig. 2, 3, 6, 7, 10) zu beobachten. Die Verschiebung der Banden erscheint nur in den Spektren der

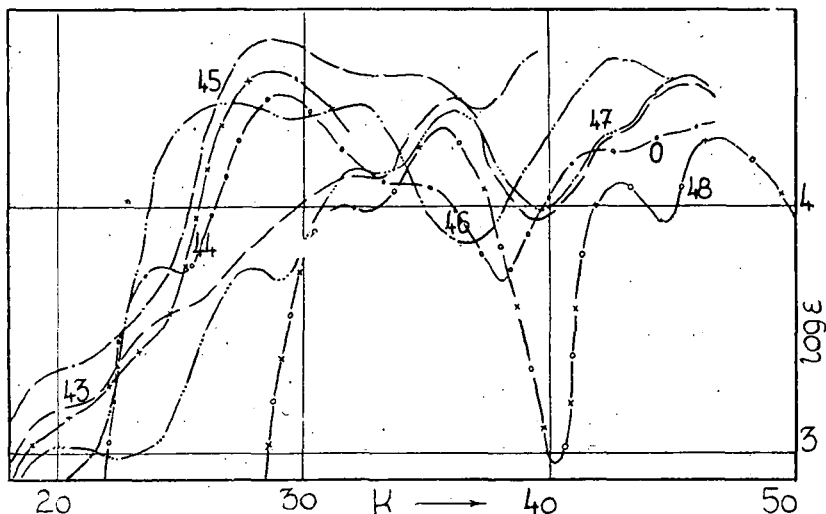


Fig. 8. Kurve 0: Resorzylaldehyd-p-anisidin in Äthanol; Fe(III) Cl-Komplex ($cc=0,00007357$)
 Kurve 43: in Äthanol; Kurve 44: in Pyridin; Kurve 45: in DMSO; Kurve 46: in 0,1n NaOH;
 Kurve 47: in 0,1n HCl; Kurve 48: Resorzylaldehyd in Äthanol.

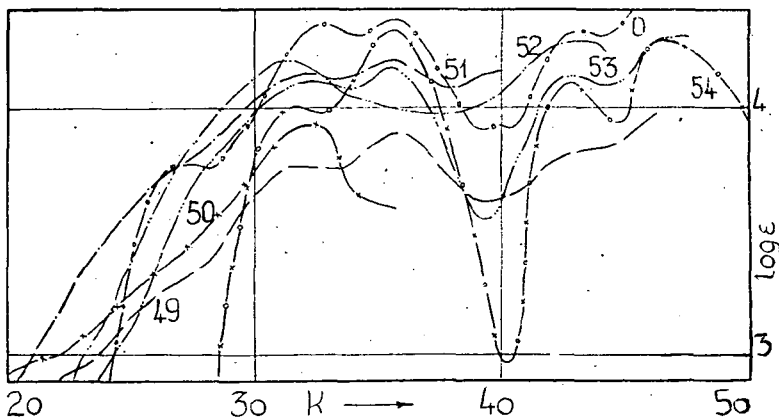


Fig. 9. Kurve 0: Resorzylaldehyd-äthylendiamin in Äthanol; Fe(III) Cl-Komplex ($cc=0,00001305$)
 Kurve 49: in Äthanol; Kurve 50: in Pyridin; Kurve 51: in DMSO; Kurve 52: in 0,1n NaOH;
 Kurve 53: in 0,1n HCl; Kurve 54: Resorzylaldehyd in Äthanol.

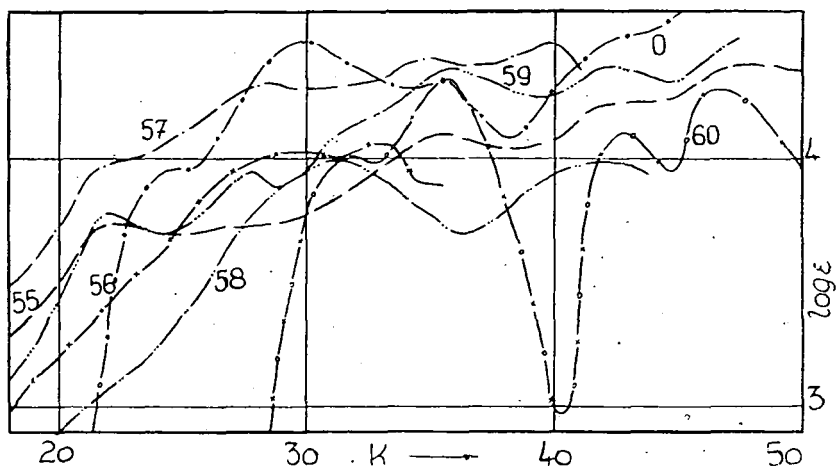


Fig. 10. Kurve 0: Resorzylaldehyd-m-phenylendiamin in Äthanol; Fe(III) Cl-Komplex ($\epsilon = 0,0000733$) Kurve 55: in Äthanol; Kurve 56: in Pyridin; Kurve 57: in DMSO; Kurve 58: in 0,1n NaOH; Kurve 59: in 0,1n HCl; Kurve 60: Resorzylaldehyd in Äthanol.

Basischen Lösungen (Fig. 1—3, 5—8) in langwelliger Richtung. In diesen Lösungsmitteln sind die Banden in einigen Fällen (Fig. 4, 9, 10) ziemlich verwaschen. Dagegen erscheinen charakteristische Banden in beiden Lösungen bei 320 mμ und 236 mμ.

* * *

Dem Leiter des Institutes, Herrn Dozenten Dr. F. MÁRTA bin ich für seine prinzipiellen Ratschläge und die Unterstützung meiner Arbeit zu aufrichtigem Danke verpflichtet.

ИЗУЧЕНИЕ Fe(III)-КОМПЛЕКСОВ АРОМАТИЧЕСКИХ ШИФФ-БАЗ. V

Серия ресорцилальдегида.

Й. Балог

Авторами изучался Fe(III) комплекс Шифф-база ресорцилальдегида с ароматическими аминами. 10 различных новых Fe(III)-хелатных комплексов описаны посредством данных анализа и значений т. п. Структура спектров полученных при 200—1200 mμ в спиртовых пиридиновых и ДМСО растворах обуславливает ковалентные связи. Но полосы переходов $d-d$ не могут быть обнаружены с полной точностью.

Комплексы показывают различную чувствительность на щелочь и окислы. Комплексы содержащие аминоэтанол и м-фенилендиамин падают на составные части и получается спектр подобен на свободный альдегид. Все таки большинство не изменяется и дает структуру подобную на спектр комплекса в спирте.

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INDUCED REACTIONS WITHIN THE PEROXY COMPOUNDS. II

Effect of Foreign Substances on the Induced Reaction Occurring in the $\text{H}_2\text{O}_2\text{—H}_2\text{S}_2\text{O}_8\text{—KMnO}_4$ System

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The effect of foreign ions on the induced reaction occurring in the $\text{H}_2\text{O}_2\text{—H}_2\text{S}_2\text{O}_8\text{—KMnO}_4$ (and $\text{—Ce(SO}_4)_2$, resp.) system was studied and found that the induced error is increased by silver (I)-, copper (II)- and iron (III)-ions, while decreased by alkali-, alkali earth metal ions, tin (IV), lead (II), chromium (III), nickel (II), cobalt (II), cerium (III)-, molybdate and tungstate-ion and especially by halide ions.

Preliminary observations [1] clearly showed that the induced reaction occurring during oxidimetric titration of hydrogen peroxide in presence of peroxydisulphate may be considerably influenced by foreign substances. The influence may be either positive or negative. In this paper we compile the results of detailed study of the effect of foreign substances on the induced reaction.

Experimental

Substances used for the measurements were all chemicals of c. p. degree. Some substances needed to be purified in spite of the c. p. qualification. Besides the customary methods if the quality of the substances made this possible, d'ANS and MATTER's [2] method was applied, too.

In a previous paper [3] it was described, how the induced reaction in the $\text{H}_2\text{O}_2\text{—H}_2\text{S}_2\text{O}_8\text{—KMnO}_4$ system depends on the experimental conditions. The knowledge of this made possible to choose such experimental conditions for the study of the foreign substances which, on the one hand assured quite a considerable induced error and satisfactory reproducibility on the other. Measurements were performed in the following manner: 5 ml 2% nitric acid and 10 ml 0,1 N peroxydisulphate and salt solutions to be investigated were measured into an Erlenmeyer flask of 250 ml volume and filled up with water to 60 ml initial volume. Immediately before titration 10 ml 0,1 N hydrogen peroxide was added and by vigorous shaking and at constant delivery rate hydrogen peroxide was titrated with permanganate. At each measurement the time of titration was 120 ± 10 sec. After the titration of hydrogen peroxide the amount of peroxydisulphate was determined, too. The applied method was described earlier [4]. According to the measurements the $\text{H}_2\text{S}_2\text{O}_8$ -error agreed in each case with the H_2O_2 -error, therefore the presentation of the peroxydisulphate data is not necessary.

Experimental results

According to the measurements alkali metal ions slightly decrease the induced error (Table I).

Table I

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|---|-----------------|--|-------------|--|
| Li ₂ SO ₄ | 0,00 | 10,10 | 9,29 | 0,81 |
| | 0,075 | 10,10 | 9,29 | 0,81 |
| | 0,15 | 10,10 | 9,30 | 0,80 |
| | 0,45 | 10,10 | 9,35 | 0,75 |
| | 0,75 | 10,10 | 9,43 | 0,67 |
| Na ₂ SO ₄ | 0,00 | 10,09 | 9,25 | 0,84 |
| | 0,055 | 10,09 | 9,27 | 0,82 |
| | 0,110 | 10,09 | 9,28 | 0,81 |
| | 0,330 | 10,09 | 9,33 | 0,76 |
| | 0,550 | 10,09 | 9,38 | 0,71 |
| K ₂ SO ₄ | 0,00 | 9,97 | 9,12 | 0,85 |
| | 0,048 | 9,97 | 9,12 | 0,85 |
| | 0,096 | 9,97 | 9,15 | 0,82 |
| | 0,288 | 9,97 | 9,24 | 0,73 |
| | 0,480 | 9,97 | 9,26 | 0,71 |
| (H ₄ N) ₂ SO ₄ | 0,00 | 10,05 | 9,20 | 0,85 |
| | 0,063 | 10,05 | 9,39 | 0,66 |
| | 0,126 | 10,05 | 9,44 | 0,61 |
| | 0,378 | 10,05 | 9,57 | 0,48 |
| | 0,630 | 10,05 | 9,76 | 0,29 |

Alkali earth metal ions bring about the decrease of the induced reaction (Table II).

Table II

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|-----------------------------------|-----------------|--|-------------|--|
| Ca(NO ₃) ₂ | 0,00 | 9,25 | 8,55 | 0,70 |
| | 0,035 | 9,25 | 8,55 | 0,70 |
| | 0,070 | 9,25 | 8,70 | 0,55 |
| | 0,210 | 9,25 | 8,75 | 0,50 |
| | 0,350 | 9,25 | 8,80 | 0,45 |
| Sr(NO ₃) ₂ | 0,00 | 10,05 | 9,30 | 0,75 |
| | 0,038 | 10,05 | 9,40 | 0,65 |
| | 0,076 | 10,05 | 9,50 | 0,55 |
| | 0,228 | 10,05 | 9,65 | 0,40 |
| | 0,380 | 10,05 | 9,70 | 0,35 |
| Ba(NO ₃) ₂ | 0,00 | 9,25 | 8,45 | 0,80 |
| | 0,030 | 9,25 | 8,60 | 0,65 |
| | 0,060 | 9,25 | 8,70 | 0,55 |
| | 0,180 | 9,25 | 8,75 | 0,50 |
| | 0,30 | 9,25 | 8,80 | 0,45 |

Elements of the zinc group increased the induced error even after the most various purifications (Table III).

Table III

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|--------------------------------------|-----------------|--|-------------|--|
| BeSO ₄ | 0,00 | 10,07 | 9,35 | 0,72 |
| | 0,0235 | 10,07 | 9,10 | 0,97 |
| | 0,0470 | 10,07 | 8,90 | 1,17 |
| | 0,0705 | 10,07 | 8,60 | 1,47 |
| | 0,0940 | 10,07 | 8,25 | 1,82 |
| | 0,2820 | 10,07 | 8,05 | 2,02 |
| Mg(NO ₃) ₂ | 0,00 | 10,10 | 9,50 | 0,60 |
| | 0,030 | 10,10 | 9,65 | 0,45 |
| | 0,060 | 10,10 | 9,70 | 0,40 |
| | 0,180 | 10,10 | 9,75 | 0,35 |
| | 0,300 | 10,10 | 9,85 | 0,25 |
| ZnSO ₄ (Chinoïn c. p.) | 0,00 | 10,10 | 9,35 | 0,75 |
| | 0,028 | 10,10 | 8,65 | 1,45 |
| | 0,056 | 10,10 | 8,35 | 1,75 |
| | 0,168 | 10,10 | 8,15 | 1,95 |
| | 0,280 | 10,10 | 7,90 | 2,20 |
| ZnSO ₄ (Merck c. p.) | 0,00 | 10,10 | 9,35 | 0,75 |
| | 0,028 | 10,10 | 9,15 | 0,95 |
| | 0,056 | 10,10 | 9,00 | 1,10 |
| | 0,168 | 10,10 | 8,85 | 1,25 |
| | 0,280 | 10,10 | 8,70 | 1,40 |
| CdSO ₄ | 0,00 | 10,23 | 9,57 | 0,66 |
| | 0,037 | 10,23 | 9,55 | 0,68 |
| | 0,074 | 10,23 | 9,53 | 0,70 |
| | 0,222 | 10,23 | 9,48 | 0,75 |
| | 0,370 | 10,23 | 9,43 | 0,80 |
| Hg(NO ₃) ₂ | 0,00 | 10,23 | 9,56 | 0,67 |
| | 0,025 | 10,23 | 9,45 | 0,78 |
| | 0,050 | 10,23 | 9,40 | 0,83 |
| | 0,150 | 10,23 | 9,37 | 0,86 |
| | 0,250 | 10,23 | 9,32 | 0,91 |

Boric acid, aluminium(III)-, thallium(III)-, cerium(III)-sulphate scarcely influenced the induced reaction or decreased it only to a small extent (Table IV).

Table IV

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|--------------------------------|-----------------|--|-------------|--|
| H ₃ BO ₃ | 0,00 | 10,05 | 9,37 | 0,68 |
| | 0,133 | 10,05 | 9,40 | 0,65 |
| | 0,266 | 10,05 | 9,43 | 0,62 |
| | 0,798 | 10,05 | 9,45 | 0,60 |
| | 1,330 | 10,05 | 9,50 | 0,55 |

Table IV

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|---|-----------------|--|-------------|--|
| Al ₂ (SO ₄) ₃ | 0,00 | 9,82 | 8,97 | 0,85 |
| | 0,023 | 9,82 | 8,98 | 0,84 |
| | 0,046 | 9,82 | 8,97 | 0,85 |
| | 0,138 | 9,82 | 8,97 | 0,85 |
| | 0,230 | 9,82 | 8,97 | 0,85 |
| Ti ₂ (SO ₄) ₃ | 0,00 | 10,05 | 9,35 | 0,70 |
| | 0,010 | 10,05 | 9,37 | 0,68 |
| | 0,020 | 10,05 | 9,37 | 0,68 |
| | 0,060 | 10,05 | 9,37 | 0,68 |
| | 0,100 | 10,05 | 9,40 | 0,65 |
| Ce ₂ (SO ₄) ₃ | 0,00 | 10,08 | 9,40 | 0,68 |
| | 0,010 | 10,08 | 9,43 | 0,65 |
| | 0,020 | 10,08 | 9,45 | 0,63 |
| | 0,040 | 10,08 | 9,48 | 0,60 |
| | 0,050 | 10,08 | 9,52 | 0,56 |
| | 0,100 | 10,08 | 9,55 | 0,53 |
| | 0,250 | 10,08 | 9,75 | 0,33 |

Tin(IV)- and lead (II)-nitrate, sodium metasilicate decrease the induced error. Arsenate ions, bismuth(III)-nitrate similarly lead to the decrease of the error (Table V).

Table V

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|-----------------------------------|-----------------|--|-------------|--|
| Sn(NO ₃) ₄ | 0,00 | 10,05 | 9,33 | 0,72 |
| | 0,021 | 10,05 | 9,45 | 0,60 |
| | 0,042 | 10,05 | 9,60 | 0,45 |
| | 0,126 | 10,05 | 9,75 | 0,30 |
| | 0,210 | 10,05 | 9,87 | 0,18 |
| Pb(NO ₃) ₂ | 0,00 | 10,05 | 9,35 | 0,70 |
| | 0,025 | 10,05 | 9,55 | 0,50 |
| | 0,050 | 10,05 | 9,68 | 0,37 |
| | 0,150 | 10,05 | 9,76 | 0,29 |
| | 0,250 | 10,05 | 9,85 | 0,20 |
| Na ₂ SiO ₃ | 0,00 | 10,07 | 9,35 | 0,72 |
| | 0,029 | 10,07 | 9,45 | 0,62 |
| | 0,058 | 10,07 | 9,65 | 0,42 |
| | 0,174 | 10,07 | 9,80 | 0,27 |
| | 0,290 | 10,07 | 9,95 | 0,12 |
| Na ₂ HAsO ₄ | 0,00 | 10,05 | 9,35 | 0,70 |
| | 0,026 | 10,05 | 9,45 | 0,60 |
| | 0,052 | 10,05 | 9,50 | 0,55 |
| | 0,156 | 10,05 | 9,65 | 0,40 |
| | 0,260 | 10,05 | 9,70 | 0,35 |
| Bi(NO ₃) ₃ | 0,00 | 10,05 | 9,30 | 0,75 |
| | 0,0167 | 10,05 | 9,40 | 0,65 |
| | 0,0334 | 10,05 | 9,50 | 0,55 |
| | 0,1002 | 10,05 | 9,57 | 0,48 |
| | 0,1670 | 10,05 | 9,63 | 0,42 |

Sulphate and selenate ions have error-decreasing effect. Chromium(III)-sulphate, molybdate, tungstate and vanadate-ions similarly cause the decrease of the error (Table VI).

Table VI

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml. | Δ H ₂ O ₂ ml |
|---|-----------------|--|--------------|--|
| Na ₂ SO ₄ | 0,00 | 10,09 | 9,25 | 0,84 |
| | 0,055 | 10,09 | 9,27 | 0,82 |
| | 0,110 | 10,09 | 9,28 | 0,81 |
| | 0,330 | 10,09 | 9,33 | 0,76 |
| | 0,550 | 10,09 | 9,38 | 0,71 |
| Na ₂ SeO ₄ | 0,00 | 9,97 | 9,25 | 0,72 |
| | 0,044 | 9,97 | 9,27 | 0,70 |
| | 0,088 | 9,97 | 9,35 | 0,62 |
| | 0,264 | 9,97 | 9,45 | 0,52 |
| | 0,440 | 9,97 | 9,56 | 0,41 |
| Cr ₂ (SO ₄) ₃ | 0,00 | 10,10 | 9,35 | 0,75 |
| | 0,021 | 10,10 | 9,40 | 0,70 |
| | 0,042 | 10,10 | 9,47 | 0,63 |
| | 0,126 | 10,10 | 9,54 | 0,56 |
| | 0,210 | 10,10 | 9,63 | 0,47 |
| Na ₂ MoO ₄ | 0,00 | 9,93 | 9,25 | 0,68 |
| | 0,034 | 9,93 | 9,70 | 0,23 |
| | 0,068 | 9,93 | 9,78 | 0,15 |
| | 0,204 | 9,93 | 9,84 | 0,09 |
| | 0,340 | 9,93 | 9,96 | 0,07 |
| Na ₂ WO ₄ | 0,00 | 10,06 | 9,35 | 0,71 |
| | 0,028 | 10,06 | 9,45 | 0,61 |
| | 0,056 | 10,06 | 9,57 | 0,49 |
| | 0,168 | 10,06 | 9,63 | 0,43 |
| | 0,280 | 10,06 | 9,68 | 0,38 |
| NaVO ₃ | 0,00 | 9,97 | 9,25 | 0,72 |
| | 0,034 | 9,97 | 9,30 | 0,67 |
| | 0,068 | 9,97 | 9,45 | 0,52 |
| | 0,102 | 9,97 | 9,57 | 0,40 |
| | 0,136 | 9,97 | 9,65 | 0,32 |
| | 0,272 | 9,97 | 9,75 | 0,22 |

Manganese(II)-ions, especially in greater quantity, exert strong error-decreasing effect. Iron(III)-ions, on the contrary, increase the error. The effect of iron(III)-ions is especially considerable when containing small quantity of iron(II)-ions, too (Table VII).

Table VII

| | Conc. mole/l | Taken 0.1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|--|-----------------|--|-------------|--|
| Mn(NO ₃) ₂ | 0,00 | 9,85 | 8,95 | 0,90 |
| | 0,033 | 9,85 | 9,10 | 0,75 |
| | 0,066 | 9,85 | 9,25 | 0,60 |
| | 0,198 | 9,85 | 9,30 | 0,55 |
| | 0,330 | 9,85 | 9,55 | 0,30 |
| MnSO ₄ | 0,00 | 10,10 | 9,35 | 0,75 |
| | 0,036 | 10,10 | 9,70 | 0,40 |
| | 0,072 | 10,10 | 9,85 | 0,25 |
| | 0,216 | 10,10 | 9,90 | 0,20 |
| | 0,360 | 10,10 | — | — |
| Fe(SO ₄) ₃ | 0,00 | 10,15 | 9,45 | 0,70 |
| | 0,010 | 10,15 | 9,40 | 0,75 |
| | 0,020 | 10,15 | 9,35 | 0,80 |
| | 0,040 | 10,15 | 9,20 | 0,95 |
| | 0,060 | 10,15 | 9,13 | 1,02 |
| | 0,080 | 10,15 | 9,02 | 1,13 |
| | 0,120 | 10,15 | 8,90 | 1,25 |
| | 0,160 | 10,15 | 8,75 | 1,40 |
| 60% Fe ₂ (SO ₄) ₃ + 40% FeSO ₄ | 0,00 | 10,10 | 9,35 | 0,75 |
| | 0,003 | 10,10 | 7,75 | 2,35 |
| | 0,0060 | 10,10 | 6,25 | 3,85 |
| | 0,012 | 10,10 | 4,05 | 6,05 |
| | 0,018 | 10,10 | 1,70 | 8,40 |
| | 0,0240 | 10,10 | 1,08 | 9,02 |
| | 0,030 | 10,10 | 2,00 | 8,10 |
| | 0,063 | 10,10 | 5,82 | 4,28 |
| | 0,160 | 10,10 | 7,25 | 2,85 |

The effect of iron-ions bound in a complex is opposed to that of aquo-metal ions. *E. g.* iron(II)-tri-*o*-phenantroline (ferroin) and iron(III)-hexacyanide complexes considerably decrease the induced error (Table VIII).

Table VIII

| | Drop | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|---------------------------------------|-------|--|-------------|--|
| Ferroin | 0 | 10,07 | 9,35 | 0,72 |
| | 1 | 10,07 | 9,80 | 0,27 |
| | 3 | 10,07 | 10,00 | 0,07 |
| | 5 | 10,07 | 10,05 | 0,02 |
| Conc. mole/l | | | | |
| K ₃ [Fe(CN) ₆] | 0,00 | 10,10 | 9,35 | 0,75 |
| | 0,025 | 10,10 | 9,40 | 0,70 |
| | 0,050 | 10,10 | 9,47 | 0,63 |
| | 0,100 | 10,10 | 9,52 | 0,58 |
| | 0,250 | 10,10 | 9,56 | 0,54 |

An interesting effect can be observed in presence of osmium tetroxide. Whilst the H_2O_2 -error is strongly increased, the $\text{H}_2\text{S}_2\text{O}_8$ -error decreased. Further investigations indicated clearly (it will be described in a subsequent paper) that osmic acid causes a considerable induced change even in absence of peroxydisulphate. Therefore, disregarding the H_2O_2 -error-increasing effect, it can be stated that osmium tetroxide inhibits the induced reaction occurring in the H_2O_2 — $\text{H}_2\text{S}_2\text{O}_8$ system (Table IX).

Table IX

| 0,01 M OsO_4 drop | Taken 0,1 N H_2O_2 | Found ml | $\Delta \text{H}_2\text{O}_2$ ml |
|-------------------------------|---------------------------------------|-------------|-------------------------------------|
| 0 | 10,10 | 9,35 | 0,75 |
| 1 | 10,10 | 7,95 | 2,15 |
| 2 | 10,10 | 7,35 | 2,75 |
| 4 | 10,10 | 6,95 | 3,15 |
| 6 | 10,10 | 6,55 | 3,55 |
| 8 | 10,10 | 6,25 | 3,85 |
| 10 | 10,10 | 5,95 | 4,15 |

| 0,01 N OsO_4 drop | Taken 0,1 N H_2O_2 | Found ml | $\Delta \text{H}_2\text{O}_2$ ml | $\text{H}_2\text{S}_2\text{O}_8$ ml | *Found 0,1 N H_2O_2 ml | * $\Delta \text{H}_2\text{O}_2$ ml |
|-------------------------------|---------------------------------------|-------------|-------------------------------------|--|---|---------------------------------------|
| 0 | 10,10 | 9,40 | 0,70 | 0,65 | 10,10 | — |
| 2 | 10,10 | 7,50 | 2,60 | 0,35 | 7,93 | 2,17 |
| 4 | 10,10 | 6,75 | 3,25 | 0,18 | 7,01 | 3,09 |
| 6 | 10,10 | 6,45 | 3,65 | 0,10 | 6,70 | 3,40 |
| 8 | 10,10 | 6,20 | 3,90 | 0,05 | 6,25 | 3,85 |

* Data obtained in absence of $\text{H}_2\text{S}_2\text{O}_8$.

Cobalt(II), nickel(II)-ions decrease the induced error. Uranyl ions exert similar effect. On the contrary, copper(II) and silver(I) ions increase the induced error (Table X). The effect of copper(II) ions will be discussed in the following paper.

From among halide ions fluoride increases the error and on the contrary, chloride, bromide and iodide ions inhibit the induced reaction (Table XI).

Table X

| | Conc. mole/l | Taken 0,1 N H_2O_2 | Found ml | $\Delta \text{H}_2\text{O}_2$ ml |
|----------------------------|-----------------|---------------------------------------|-------------|-------------------------------------|
| CoSO_4 | 0,00 | 10,10 | 9,35 | 0,75 |
| | 0,0296 | 10,10 | 9,43 | 0,67 |
| | 0,0592 | 10,10 | 9,47 | 0,63 |
| | 0,1776 | 10,10 | 9,55 | 0,55 |
| | 0,2960 | 10,10 | 9,63 | 0,47 |
| $\text{Ni}(\text{NO}_3)_2$ | 0,00 | 10,15 | 9,35 | 0,80 |
| | 0,026 | 10,15 | 9,40 | 0,75 |
| | 0,052 | 10,15 | 9,45 | 0,70 |
| | 0,162 | 10,15 | 9,55 | 0,62 |
| | 0,260 | 10,15 | 9,60 | 0,55 |

Table X

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|---|-----------------|--|-------------|--|
| UO ₂ (NO ₃) ₂ | 0,00 | 9,93 | 9,25 | 0,68 |
| | 0,008 | 9,93 | 9,75 | 0,18 |
| | 0,016 | 9,93 | 9,80 | 0,13 |
| | 0,032 | 9,93 | 9,86 | 0,07 |
| | 0,064 | 9,93 | 9,90 | 0,03 |
| | | | | |
| CuSO ₄ | 0,00 | 10,15 | 9,35 | 0,70 |
| | 0,000066 | 10,15 | 4,90 | 5,25 |
| | 0,00066 | 10,15 | 4,55 | 5,60 |
| | 0,0033 | 10,15 | 4,25 | 5,90 |
| | 0,0066 | 10,15 | 4,00 | 6,15 |
| | 0,0165 | 10,15 | 3,78 | 6,37 |
| | 0,033 | 10,15 | 4,70 | 5,45 |
| | 0,066 | 10,15 | 5,20 | 4,95 |
| | 0,198 | 10,15 | 6,20 | 3,95 |
| | 0,330 | 10,15 | 7,80 | 2,35 |
| AgNO ₃ | 0,00 | 9,76 | 9,05 | 0,71 |
| | 0,000096 | 9,76 | 8,75 | 1,01 |
| | 0,00096 | 9,76 | 8,35 | 1,41 |
| | 0,0096 | 9,76 | 7,95 | 1,81 |
| | 0,048 | 9,76 | 7,50 | 2,26 |
| | 0,096 | 9,76 | 6,40 | 3,36 |
| | 0,288 | 9,76 | 4,25 | 5,51 |
| | 0,480 | 9,76 | 3,25 | 6,51 |

Table XI

| | Conc. mole/l | Taken 0,1 N H ₂ O ₂ | Found ml | Δ H ₂ O ₂ ml |
|------|-----------------|--|-------------|--|
| NaF | 0,00 | 10,06 | 9,41 | 0,65 |
| | 0,0015 | 10,06 | 9,39 | 0,67 |
| | 0,0039 | 10,06 | 9,37 | 0,69 |
| | 0,0078 | 10,06 | 9,33 | 0,73 |
| | 0,0234 | 10,06 | 9,10 | 0,96 |
| | 0,039 | 10,06 | 8,89 | 1,17 |
| | | | | |
| NaCl | 0,00 | 10,05 | 9,36 | 0,69 |
| | 0,029 | 10,05 | 9,55 | 0,50 |
| | 0,145 | 10,05 | 9,90 | 0,15 |
| | 0,290 | 10,05 | 10,05 | 0,00 |
| NaBr | 0,00 | 9,99 | 9,28 | 0,71 |
| | 0,0009 | 9,99 | 9,40 | 0,59 |
| | 0,0018 | 9,99 | 9,45 | 0,54 |
| | 0,0044 | 9,99 | 9,58 | 0,41 |
| | 0,0090 | 9,99 | 9,65 | 0,34 |
| | 0,0180 | 9,99 | 9,75 | 0,24 |
| | 0,0600 | 9,99 | 9,90 | 0,09 |
| NaJ | 0,00 | 9,99 | 9,27 | 0,72 |
| | 0,0011 | 9,99 | 9,82 | 0,17 |
| | 0,0035 | 9,99 | 9,96 | 0,03 |

On summarizing the results the studied ions can be divided into two groups regarding their effect:

I. The induced error is increased by: Cu(II), Ag(I), Be(II), Zn(II), Cd(II), Hg(II), Fe(III) ions. From among anions fluoride has an error increasing effect.

II. The induced error is decreased by: Na, K, Mg, Ca, Sr, Na, Sn(IV), Pb(II), Bi(III), Cr(III), Ce(III), Al(III), Ti(III), Co(II), Ni(II) ions. From among anions metasilicate, phosphate, arsenate, sulphate, selenate, molybdenate, tungstate, borate and ferricyanide also decrease the error.

Ammonium, uranyl, manganese(II) ions exert a strong error-decreasing effect similarly as from among anions chloride, bromide, iodide and acetate ions do.

Interpretation of the above described effects will be found elsewhere [3].

* * *

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ИНДУКЦИОННЫЕ РЕАКЦИИ СРЕДИ ПЕРОКСИ-СОЕДИНЕНИЙ. II

Действие посторонних веществ на реакцию в системе $H_2O_2-H_2S_2O_8-KMnO_4$

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Действие посторонних ионов на индукционную реакцию в системе



было изучено и установлено что индукционная ошибка увеличивается под воздействием ионов серебра (I), меди (II), железа (III), и она уменьшается под эффектом ионов щелочи, щелочноземельных металлов, олова (IV), свинца (II), хрома (III), никеля (II) кобальта (II), церия (III), молибдата (VI), и вольфрамата (VI), и очень значительно галогидных ионов.

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INDUCED REACTIONS WITHIN THE PEROXY COMPOUNDS. III

Copper(II)-Ion Catalysis of the Induced Reaction Occurring in the $\text{H}_2\text{O}_2\text{--H}_2\text{S}_2\text{O}_8\text{--Ce}(\text{SO}_4)_2$ System

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The effect of copper (II) ion exerted on the induced reaction occurring in the $\text{H}_2\text{O}_2\text{--H}_2\text{S}_2\text{O}_8\text{--KMnO}_4$ (and $\text{--Ce}(\text{SO}_4)_2$, resp.) system was investigated in detail and found that cupric ions do not change the properties of induced reaction, only strongly catalyze the induced change.

In Part I of this series the features of the induced reaction occurring in the $\text{H}_2\text{O}_2\text{--H}_2\text{S}_2\text{O}_8$ system were dealt with [1] and the effect of foreign substances was described in Part II. [2]. In this paper data will be delivered to prove the copper(II) ion catalysis of the induced reaction. This seems to be interesting then as far as we know there are no references in the literature concerning the catalysis of induced reactions.

Experimental

0,1 N hydrogen peroxide solution was prepared from stabilisator-free Merck Perhydrol and 0,1 N peroxydisulphate solution from Merck c. p. N-free potassium peroxydisulphate reagent. 0,1 N cerium(IV) sulphate and 0,1 N arsenous acid reagent solution were prepared from c. p. substances and standardized in the usual manner.

Measurements: 10 ml of about 0,1 N hydrogen peroxide solution was acidified with 5 ml of 20% sulphuric acid, added to it 10 ml of 0,1 N peroxydisulphate and copper(II)-sulphate solution in the required amount and then filled up to 40 ml. Thereafter by vigorous stirring hydrogen peroxide was titrated in presence of 1 drop. 0,025 M ferroin indicator with cerium(IV) sulphate, at a constant delivery rate. The titration time was 120 ± 10 sec at each measurement.

In another group of experiments (inversed titrations) cerium(IV) sulphate and peroxydisulphate solutions were poured together and titrated with about 0,1 N hydrogen peroxide solution. The acid concentration and the initial volume were as given. Having measured the hydrogen peroxide and cerium(IV) sulphate, respectively, the peroxydisulphate content was determined, too. The method was described in an earlier paper [3].

*Experimental results**I. Direct titrations*

Data of Table I show that on effect of increasing amount of copper(II)-ions the induced error increases. The change can be represented by a curve of saturation value. As it can be seen, the values of the H_2O_2 - and $\text{H}_2\text{S}_2\text{O}_8$ -error practically agree.

Table I

| Cu mg | Taken 0,1 N H_2O_2 ml | Found | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|----------|--|-------|--|-------|-------------------------------------|---|
| — | 8,58 | 7,93 | 9,29 | 8,62 | 0,65 | 0,67 |
| 0,3978 | 8,58 | 7,70 | 9,29 | 8,43 | 0,88 | 0,86 |
| 0,7956 | 8,58 | 7,20 | 9,29 | 7,88 | 1,38 | 1,41 |
| 1,5912 | 8,58 | 6,99 | 9,29 | 7,67 | 1,59 | 1,62 |
| 3,1824 | 8,58 | 6,82 | 9,29 | 7,51 | 1,76 | 1,78 |
| 6,366 | 8,58 | 6,36 | 9,29 | 7,09 | 2,22 | 2,20 |
| 7,9572 | 8,58 | 6,28 | 9,29 | 6,92 | 2,30 | 2,37 |
| 9,9462 | 8,58 | 6,23 | 9,29 | 6,88 | 2,35 | 2,41 |
| 12,732 | 8,58 | 6,28 | 9,29 | 6,88 | 2,30 | 2,41 |
| 19,098 | 8,58 | 6,23 | 9,29 | 6,92 | 2,35 | 2,37 |
| 25,464 | 8,58 | 6,28 | 9,29 | 6,88 | 2,30 | 2,41 |

At constant peroxydisulphate concentration, changing the amount of hydrogen peroxide and at constant hydrogen peroxide concentration the amount of the peroxydisulphate, respectively, the induced error increases in both instances (Table II).

Table II

| Taken 0,1 N H_2O_2 ml | Found | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|--|-------|--|-------|-------------------------------------|---|
| 1,65 | 0,84 | 7,86 | 7,19 | 0,81 | 0,67 |
| 2,48 | 1,60 | 7,86 | 6,94 | 0,88 | 0,92 |
| 3,31 | 2,30 | 7,86 | 6,87 | 1,01 | 0,99 |
| 4,14 | 3,05 | 7,86 | 6,77 | 1,09 | 1,09 |
| 4,97 | 3,64 | 7,86 | 6,64 | 1,33 | 1,22 |
| 6,63 | 5,10 | 7,86 | 6,19 | 1,53 | 1,67 |
| 8,29 | 6,73 | 7,86 | 6,09 | 1,56 | 1,77 |
| 11,60 | 9,54 | 7,86 | 5,91 | 2,06 | 1,95 |
| 13,25 | 11,05 | 7,86 | 5,84 | 2,20 | 2,02 |
| 14,91 | 12,76 | 7,86 | 5,72 | 2,15 | 2,14 |
| 16,57 | 14,27 | 7,86 | 5,69 | 2,30 | 2,17 |
| 8,87 | 8,24 | 1,61 | 0,92 | 0,63 | 0,69 |
| 8,87 | 7,87 | 3,21 | 1,93 | 1,00 | 1,28 |
| 8,87 | 7,45 | 4,82 | 3,31 | 1,42 | 1,51 |
| 8,87 | 7,19 | 6,43 | 4,64 | 1,68 | 1,79 |
| 8,87 | 6,95 | 8,03 | 5,80 | 1,92 | 2,23 |
| 8,87 | 6,36 | 11,24 | 8,50 | 2,51 | 2,74 |
| 8,87 | 6,11 | 12,85 | 9,92 | 2,76 | 2,93 |
| 8,87 | 6,02 | 14,46 | 11,60 | 2,85 | 2,86 |
| 8,87 | 5,77 | 16,07 | 12,93 | 3,10 | 3,14 |

Each sample contains 2,38 mg Cu(II)-ion.

Increasing the acid concentration the induced error decreases (Table III).

Table III

| 20% H_2SO_4 ml | Taken 0,1 N H_2O_2 ml | Found ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found ml | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|-----------------------------------|--|-------------|--|-------------|-------------------------------------|---|
| 3 | 8,33 | 6,03 | 7,87 | 5,65 | 2,30 | 2,22 |
| 5 | 8,33 | 6,57 | 7,87 | 6,03 | 1,76 | 1,84 |
| 10 | 8,33 | 6,65 | 7,87 | 6,15 | 1,68 | 1,72 |
| 15 | 8,33 | 6,86 | 7,87 | 6,44 | 1,47 | 1,43 |
| 20 | 8,33 | 6,99 | 7,87 | 6,44 | 1,34 | 1,43 |

Reducing the speed of titration the induced error increases (Table IV).

Table IV

| Time sec | Taken 0,1 N H_2O_2 ml | Found ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found ml | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|-------------|--|-------------|--|-------------|-------------------------------------|---|
| 20 | 8,47 | 6,61 | 7,99 | 6,13 | 1,86 | 1,86 |
| 35 | 8,47 | 6,56 | 7,99 | 6,13 | 1,91 | 1,86 |
| 39 | 8,47 | 6,52 | 7,99 | 6,04 | 1,95 | 1,95 |
| 70 | 8,47 | 6,47 | 7,99 | 6,00 | 2,00 | 1,99 |
| 120 | 8,47 | 6,42 | 7,99 | 5,90 | 2,05 | 2,09 |
| 245 | 8,47 | 6,32 | 7,99 | 5,82 | 2,15 | 2,17 |
| 289 | 8,47 | 6,27 | 7,99 | 5,79 | 2,20 | 2,20 |
| 363 | 8,47 | 6,22 | 7,99 | 5,72 | 2,25 | 2,27 |

Each sample contains 2,38 mg Cu(II) ion.

On increasing the dilution of the titrated solution — maintaining the acid and the copper(II)-ion concentration constant — the error increases (Table V).

Table V

| Volume ml | Taken 0,1 N H_2O_2 ml | Found ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found ml | Cu mg | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|--------------|--|-------------|--|-------------|----------|-------------------------------------|---|
| 25 | 6,28 | 1,53 | 8,64 | 7,16 | 7,95 | 1,53 | 1,48 |
| 50 | 6,28 | 1,73 | 8,64 | 7,00 | 15,90 | 1,73 | 1,64 |
| 100 | 6,28 | 1,96 | 8,64 | 6,72 | 31,80 | 1,96 | 1,92 |
| 150 | 6,28 | 2,12 | 8,64 | 6,56 | 47,70 | 2,12 | 2,08 |
| 200 | 6,28 | 2,18 | 8,64 | 6,52 | 63,60 | 2,18 | 2,12 |

On the effect of cerium(III) nitrate the induced reaction slightly increases (Table VI).

Table VI

| $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ g | Taken 0,1 N H_2O_2 ml | Found | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|---|--|-------|--|-------|-------------------------------------|---|
| — | 9,63 | 7,50 | 9,75 | 7,52 | 2,13 | 2,23 |
| 0,086 | 9,63 | 7,50 | 9,75 | 7,50 | 2,13 | 2,25 |
| 0,086 | 9,63 | 7,45 | 9,75 | 7,52 | 2,18 | 2,23 |
| 0,434 | 9,63 | 7,42 | 9,75 | 7,40 | 2,21 | 2,35 |
| 0,434 | 9,63 | 7,40 | 9,75 | 7,42 | 2,23 | 2,33 |
| 0,860 | 9,63 | 7,28 | 9,75 | 7,20 | 2,35 | 2,55 |
| 1,500 | 10,20 | 7,30 | 9,60 | — | 2,90 | — |
| 2,170 | 9,63 | 6,50 | 9,75 | — | 3,13 | — |
| 2,170 | 9,63 | 6,50 | 9,75 | 6,50 | 3,13 | 3,25 |

Each sample contains 12,732 mg Cu(II) ion.

When adding fluoride ions the induced error increases, however, it decreases in presence of chloride, bromide and iodide ions (Table VII).

Table VII

| Fluoride mg | Taken 0,1N H_2O_2 ml | Found | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|------------------|---|-------|--|-------|-------------------------------------|---|
| — | 9,35 | 9,12 | 10,53 | 10,25 | 0,23 | 0,28 |
| — | 9,35 | 6,98 | 10,53 | 17,98 | 2,37 | 2,55 |
| 1,90 | 9,35 | 5,65 | 10,53 | 7,30 | 3,70 | 3,23 |
| 3,80 | 9,35 | 4,80 | 10,53 | — | 4,55 | — |
| 3,80 | 9,35 | 9,30 | — | — | 0,05 | — |
| 38,0 | 9,35 | 9,80 | — | — | +0,45 | — |
| 38,0 | 9,35 | 2,83 | 10,53 | 3,90 | 6,52 | 6,63 |
| 3,80 | 9,35 | 3,21 | 10,53 | 4,45 | 6,14 | 6,08 |
| 1,90 | 9,35 | 4,03 | 10,53 | 5,15 | 5,32 | 5,38 |
| 0,95 | 9,35 | 5,03 | 10,53 | 6,20 | 4,32 | 4,43 |
| 19,00 | 9,35 | 3,05 | 10,53 | 4,15 | 6,30 | 6,38 |
| 28,50 | 9,35 | 2,88 | 10,53 | 4,05 | 6,47 | 6,48 |
| Chloride mmole/l | | | | | | |
| — | 10,03 | 7,85 | 11,73 | 9,53 | 2,18 | 2,20 |
| 0,570 | 10,03 | 8,60 | 11,73 | 10,18 | 1,43 | 1,55 |
| 2,850 | 10,03 | 9,50 | 11,73 | 11,08 | 0,53 | 0,65 |
| 5,700 | 10,03 | 9,65 | 11,73 | 11,20 | 0,38 | 0,53 |
| Bromide mmole/l | | | | | | |
| 0,250 | 10,03 | 8,95 | 11,73 | 10,63 | 1,08 | 1,10 |
| 1,250 | 10,03 | 9,40 | 11,73 | 11,08 | 0,63 | 0,65 |
| 2,500 | 10,03 | 9,75 | 11,73 | 11,58 | 0,28 | 0,15 |
| Iodide mmole/l | | | | | | |
| 0,157 | 10,03 | 9,05 | 11,73 | 10,85 | 0,98 | 0,88 |
| 0,785 | 10,03 | 9,45 | 11,73 | 11,28 | 0,58 | 0,45 |
| 1,570 | 10,03 | 10,00 | 11,73 | 12,65 | 0,03 | +0,92 |

Samples contain 12,73mg Cu(II) ion except the first one.

If besides hydrogen peroxide and peroxydisulphate the solution contains arsenous acid, too, the H_2O_2 -error markedly decreases, the $\text{H}_2\text{S}_2\text{O}_8$ -error remains practically unchanged and the amount of arsenite becomes erroneous, too (Table

VIII). The value of As_2O_3 -error equals to the sum of the H_2O_2 - and $\text{H}_2\text{S}_2\text{O}_8$ -errors.

Table VIII

| No | Taken 0,1 N H_2O_2 ml | Found | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | Taken 0,1 N As_2O_3 ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml | $\Delta \text{As}_2\text{O}_3$ ml |
|----|--|-------|--|-------|---|-------|-------------------------------------|---|--------------------------------------|
| 1 | 8,62 | 8,48 | 10,23 | 9,25 | 10,23 | 9,00 | 0,14 | 0,98 | 1,23 |
| 2 | 8,62 | 8,20 | 10,23 | 8,49 | 10,23 | 8,03 | 0,42 | 1,74 | 2,20 |
| 3 | 8,62 | 8,20 | 10,23 | 7,95 | 10,23 | 7,45 | 0,42 | 2,28 | 2,78 |
| 4 | 8,62 | 8,16 | 10,23 | 7,63 | 10,23 | 7,18 | 0,46 | 2,60 | 3,05 |
| 5 | 8,62 | 8,03 | 10,23 | 6,16 | 10,23 | 6,65 | 0,59 | 3,07 | 3,58 |
| 6 | 8,81 | 8,30 | 9,83 | 6,38 | 10,23 | 6,28 | 0,51 | 3,44 | 3,95 |
| 7 | 8,81 | 8,18 | 9,83 | 6,17 | 10,23 | 5,96 | 0,63 | 3,66 | 4,27 |
| 8 | 8,81 | 8,03 | 9,83 | 5,69 | 10,23 | 5,31 | 0,78 | 4,14 | 4,92 |
| 9 | 8,81 | 7,95 | 9,83 | 5,65 | 10,23 | 5,31 | 0,86 | 4,18 | 4,92 |

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|------------------|--------|--------|-------|-------|-------|-------|-------|-------|-------|
| Cu mg/ sample | 0,3978 | 0,7956 | 1,591 | 3,182 | 6,366 | 12,73 | 25,46 | 50,92 | 63,65 |

II. Inverse titrations

As it appears from Table IX, inverse titrations furnish practically correct hydrogen peroxide values, however, some error appears in the amount of peroxy-

Table IX

| Taken 0,1 N $\text{Ce}(\text{SO}_4)_2$ ml | Consumed 0,1 N H_2O_2 ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | Taken 0,1 N As_2O_3 ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml | $\Delta \text{As}_2\text{O}_3$ ml | Ferroin drop |
|---|--|--|-------|---|-------|-------------------------------------|---|--------------------------------------|-----------------|
| 10,10 | 10,15 | 10,80 | 10,70 | — | — | +0,05 | -0,10 | — | 1 |
| 10,10 | 10,12 | 10,80 | 10,75 | — | — | +0,02 | -0,05 | — | 1 |
| 10,10 | 10,15 | 10,80 | 10,75 | — | — | +0,05 | -0,05 | — | 1 |
| 10,10 | 10,10 | 10,80 | 10,70 | — | — | 0,00 | -0,10 | — | 1 |
| 10,10 | 10,15 | 10,80 | 10,75 | — | — | +0,05 | -0,05 | — | — |
| 10,10 | 10,20 | 10,80 | 10,75 | — | — | +0,10 | -0,05 | — | — |
| 10,10 | 10,15 | 10,80 | 10,70 | — | — | +0,05 | -0,10 | — | — |
| 10,10 | 10,12 | 10,80 | 10,78 | — | — | +0,02 | -0,02 | — | — |
| 10,10 | 9,92 | 10,80 | 10,60 | 10,20 | 9,75 | -0,18 | -0,20 | -0,45 | 1 |
| 10,10 | 9,93 | 10,80 | 10,55 | 10,20 | 9,70 | -0,17 | -0,25 | -0,50 | 1 |
| 10,10 | 9,90 | 10,80 | 10,40 | 10,20 | 9,80 | -0,20 | -0,40 | -0,40 | 1 |
| 10,10 | 9,92 | 10,80 | 10,50 | 10,20 | 9,75 | -0,18 | -0,30 | -0,45 | 1 |
| 10,10 | 9,90 | 10,80 | 10,65 | 10,20 | 9,80 | -0,20 | -0,15 | -0,40 | — |
| 10,10 | 9,92 | 10,80 | 10,60 | 10,20 | 9,75 | -0,18 | -0,20 | -0,45 | — |
| 10,10 | 9,95 | 10,80 | 10,70 | 10,20 | 9,85 | -0,20 | -0,10 | -0,35 | — |
| 10,10 | 12,20 | 10,80 | 8,50 | — | — | +2,10 | -2,30 | — | — |
| 10,10 | 12,15 | 10,80 | 8,60 | — | — | +2,05 | -2,20 | — | — |
| 10,10 | 12,18 | 10,80 | 8,55 | — | — | +2,08 | -2,25 | — | — |
| 10,10 | 12,30 | 10,80 | 8,50 | — | — | +2,20 | -2,30 | — | — |
| 10,10 | 10,15 | 10,80 | 8,80 | 10,20 | 7,95 | +0,05 | -2,00 | -2,25 | — |
| 10,10 | 10,13 | 10,80 | 8,90 | 10,20 | 7,95 | +0,03 | -1,90 | -2,25 | — |
| 10,10 | 10,20 | 10,80 | 8,65 | 10,20 | 7,90 | +0,10 | -2,15 | -2,30 | — |
| 10,10 | 10,15 | 10,80 | 8,70 | 10,20 | 8,00 | +0,05 | -2,10 | -2,20 | — |

Each sample contains 12,73 mg Cu(II) ion.

disulphate. In presence of arsenite the H_2O_2 -error slightly increases, the $\text{H}_2\text{S}_2\text{O}_8$ -error remains unaltered and the value of the As_2O_3 -error, similarly to the direct titrations, equals to the sum of H_2O_2 - and $\text{H}_2\text{S}_2\text{O}_8$ -errors. In presence of copper(II)-ions the amount of hydrogen peroxide consumed for cerium(IV) considerably increases, and we get the peroxydisulphate-values with a greater negative error. When adding arsenous acid the positive H_2O_2 -error is greatly decreased and a negative As_2O_3 -error appears instead, the $\text{H}_2\text{S}_2\text{O}_8$ -error remains unaltered.

The increasing of the acid concentration, reduces the induced error in case of inverse titrations, too (Table X).

Table X

| 20 % H_2SO_4 ml | Taken $\text{Ce}(\text{SO}_4)_2$ 0,1 N ml | Consumed H_2O_2 0,1 N ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found ml | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|---------------------------------------|---|--|--|-------------|-------------------------------------|---|
| 3 | 9,40 | 11,50 | 11,67 | 9,34 | +2,10 | -2,33 |
| 3 | 9,48 | 11,70 | 11,75 | — | +2,22 | — |
| 5 | 9,48 | 11,50 | 11,75 | — | +2,02 | — |
| 10 | 9,40 | 11,20 | 11,67 | 9,77 | +1,80 | -1,90 |
| 15 | 9,40 | 10,83 | 11,67 | 10,07 | +1,43 | -1,60 |
| 20 | 9,40 | 10,70 | 11,67 | 10,27 | +1,30 | -1,40 |
| 20 | 9,48 | 10,95 | 11,75 | — | +1,47 | — |

The induced reaction is directly proportional to the titration speed. This is opposite to the behaviour found at direct titrations (Table XI).

Table XI

| Time sec | Taken $\text{Ce}(\text{SO}_4)_2$ 0,1 N ml | Consumed H_2O_2 0,1 N ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found ml | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|----------|---|--|--|-------------|-------------------------------------|---|
| 35 | 10,20 | 12,35 | 10,75 | 8,50 | +2,15 | -2,25 |
| 30 | 10,20 | 12,40 | 10,75 | 8,45 | +2,20 | -2,30 |
| 35 | 10,23 | 12,45 | 10,55 | 8,20 | +2,22 | -2,35 |
| 28 | 10,23 | 12,40 | 10,55 | — | +2,17 | — |
| 125 | 10,20 | 12,00 | 10,75 | 8,70 | +1,80 | -2,05 |
| 112 | 10,20 | 12,20 | 10,75 | — | +2,00 | — |
| 121 | 10,23 | 12,25 | 10,55 | 7,95 | +2,02 | -2,60 |
| 250 | 10,20 | 12,15 | 10,75 | 8,70 | +1,95 | -2,05 |
| 278 | 10,23 | 11,95 | 10,55 | 8,72 | +1,72 | -1,83 |
| 585 | 10,20 | 11,87 | 10,75 | 9,05 | +1,67 | -1,70 |
| 550 | 10,23 | 11,88 | 10,55 | 8,85 | +1,65 | -1,70 |

On diluting the solution the error increases (Table XII).

Table XII

| Volume ml | | | | | | |
|-----------|------|-------|-------|---|-------|---|
| 50 | 9,48 | 11,45 | 10,75 | — | +1,97 | — |
| 50 | 9,48 | 11,50 | 10,75 | — | +2,02 | — |
| 50 | 9,48 | 11,52 | 10,75 | — | +2,04 | — |
| 100 | 9,48 | 11,68 | 10,75 | — | +2,20 | — |

Volume ml

| | | | | | | |
|-----|------|-------|-------|---|-------|---|
| 100 | 9,48 | 11,73 | 10,75 | — | +2,25 | — |
| 200 | 9,48 | 12,05 | 10,75 | — | +2,57 | — |
| 200 | 9,48 | 12,00 | 10,75 | — | +2,52 | — |
| 300 | 9,48 | 12,38 | 10,75 | — | +2,90 | — |
| 300 | 9,48 | 12,40 | 10,75 | — | +2,92 | — |

Tables X and XI: in presence of 12,73 mg Cu/sample

Table XII in presence of 12,73 mg/50 ml.

Raising the hydrogen peroxide and peroxydisulphate concentrations the error equally increases (Table XIII).

Table XIII

| Taken $\text{Ce}(\text{SO}_4)_2$ 0,1 N ml | Consumed H_2O_2 0,1 N ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|---|--|--|-------|-------------------------------------|---|
| 2,47 | 3,45 | 12,77 | 11,65 | +0,98 | -1,12 |
| 4,95 | 6,35 | 12,77 | 11,20 | +1,43 | -1,57 |
| 9,90 | 12,00 | 12,77 | 10,55 | +2,10 | -2,22 |
| 19,80 | 22,35 | 12,77 | 10,25 | +2,55 | -2,52 |
| 49,50 | 52,40 | 12,77 | — | +2,90 | — |
| 9,90 | 10,60 | 3,19 | 2,50 | +0,70 | -0,69 |
| 9,90 | 11,10 | 6,38 | 5,25 | +1,20 | -1,13 |
| 9,90 | 11,95 | 12,77 | 10,50 | +2,05 | -2,27 |
| 9,90 | 13,30 | 25,54 | — | +3,40 | — |
| 9,90 | 16,50 | 63,85 | — | +6,60 | — |

In presence of 25,46 mg Cu/80 ml

On effect of chloride, bromide and iodide ions, just as at direct titrations, the induced error decreases. Fluoride ions increase the error here, too (Table XIV).

Table XIV

| Chloride mmole/ | Taken $\text{Ce}(\text{SO}_4)_2$ 0,1 N ml | Consumed H_2O_2 0,1 N ml | Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{H}_2\text{S}_2\text{O}_8$ ml |
|--------------------|---|--|--|-------|-------------------------------------|---|
| — | 10,00 | 12,10 | 11,80 | 9,55 | +2,10 | -2,25 |
| 0,570 | 10,00 | 11,15 | 11,80 | 10,65 | +1,15 | -1,15 |
| 2,850 | 10,00 | 10,60 | 11,80 | 11,20 | +0,60 | -0,60 |
| 5,700 | 10,00 | 10,48 | 11,80 | 11,20 | +0,48 | -0,60 |
| Bromide mmole/l | | | | | | |
| 0,250 | 10,00 | 10,90 | 11,80 | 10,75 | +0,90 | -1,05 |
| 1,250 | 10,00 | 10,55 | 11,80 | 11,15 | +0,55 | -0,65 |
| 2,500 | 10,00 | 10,35 | 11,80 | 11,60 | +0,35 | -0,20 |
| Iodide mmole/l | | | | | | |
| 0,157 | 10,00 | 10,60 | 11,80 | — | +0,60 | — |
| 0,785 | 10,00 | 10,27 | 11,80 | — | +0,27 | — |
| 1,570 | 10,00 | 10,05 | 11,80 | — | +0,05 | — |

In presence of 12,73 mg Cu/40 ml.

On adding cerium(III)-ions the error remains unchanged. On effect of ferroin indicator the extent of induced reaction decreases (Table XV).

Table XV

| $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ g | Taken $\text{Ce}(\text{SO}_4)_2$ 0,1 N ml | Consumed H_2O_2 0,1 N ml | Taken 0,1 N $\text{H}_2\text{S}_2\text{O}_8$ ml | Found | $\Delta \text{H}_2\text{O}_2$ ml | $\Delta \text{K}_2\text{S}_2\text{O}_8$ ml |
|---|---|--|--|-------|-------------------------------------|---|
| — | 10,30 | 12,40 | 11,80 | — | +2,10 | — |
| — | 10,30 | 12,45 | 11,80 | — | +2,16 | — |
| 0,086 | 9,40 | 11,50 | 11,76 | — | +2,10 | — |
| 0,086 | 9,48 | 11,50 | 11,67 | — | +2,02 | — |
| 0,434 | 10,30 | 12,50 | 11,80 | 9,50 | +2,20 | -2,30 |
| 0,520 | 9,40 | 11,60 | 11,67 | 9,34 | +2,20 | -2,33 |
| 0,868 | 9,40 | 11,55 | 11,67 | — | +2,15 | — |
| 2,170 | 10,30 | 12,52 | 11,80 | 9,75 | +2,22 | -2,05 |

Table XV

| 0,025 M Ferroin drop | Taken 0,1 N H_2O_2 ml | Found | Taken $\text{K}_2\text{S}_2\text{O}_8$ 0,1 N ml | $\Delta \text{H}_2\text{O}_2$ ml |
|----------------------------|--|-------|---|-------------------------------------|
| — | 10,08 | 6,40 | 10,10 | 3,68 |
| — | 10,08 | 6,45 | 10,10 | 3,63 |
| 1 | 10,08 | 7,70 | 10,10 | 2,38 |
| 4 | 10,08 | 8,15 | 10,10 | 1,93 |
| 9 | 10,08 | 8,75 | 10,10 | 1,33 |

In presence of 12,73 mg Cu/40 ml

III. Complications in the indication of the end point of titrations

During the direct titrations it was observed that even in case of the most carefully performed end-point determination several drops of hydrogen peroxide were required to reduce ferroin, *i. e.* in spite of the utmost care apparently the solution was overtitrated. The phenomenon is even more striking as by potentiometric control it could be established that in this case, too, ferroin indicates the equivalence point correctly. Considering the experience, too, that the induced reaction is markedly decreased on the addition of ferroin, it seems to be probable that the indicator undergoes a complex redox change, *i. e.* a reversible and partly an irreversible change, too. This can be especially clearly observed if hydrogen peroxide is titrated with permanganate using ferroin indicator instead of cerium(IV)-sulphate. In that case the colour of ferroin disappears already considerably before the permanganate end-point. Table XVI shows that the difference between the complete discolouration of the ferroin indicator and the appearance of the permanganate colour expressed in ml (values A) is the greater, the more copper(II)-ions are present in the solution. This is interesting because copper(II)-ions, in absence of peroxydisulphate do not interfere the indication of the end point at most owing to their own colour. It must be further emphasized, that after the titration the ferroin

pink colour could not be recovered even with strong reducing agents added in large quantity (such as tin(II)-chloride or iron(II)-sulphate, *etc.*) neither when the reduction is allowed to proceed for a longer time (24 hours). This clearly shows that during the induced reaction ferroin loses its indicator ability. This is supported by the experience, too, that after the destruction of indicator colour the inhibiting effect of ferroin ceases.

Table XVI

| Cu mg | Ferroin drop | Taken 0,1 N H ₂ O ₂ | Found ml | Taken K ₂ S ₂ O ₈ ml | Δ H ₂ O ₂ ml | A ml |
|-------|--------------|---|----------|---|---|------|
| 12,73 | — | 10,01 | 5,95 | 10,25 | —4,06 | — |
| 12,73 | 1 | 10,01 | 8,35 | 10,25 | —1,66 | 0,60 |
| 6,36 | 1 | 10,01 | 8,45 | 10,25 | —1,56 | 0,50 |
| 3,18 | 1 | 10,01 | 8,52 | 10,25 | —1,49 | 0,47 |
| 2,55 | 1 | 9,50 | 8,20 | 10,25 | —1,30 | 0,35 |
| 0,25 | 1 | 10,01 | 8,97 | 10,25 | —1,04 | 0,12 |
| 12,73 | 1 | 10,01 | 9,98 | — | —0,03 | — |

To a further clearing up of the question it was studied whether the inhibiting effect of the indicator is connected with the complex itself or with the ligand molecule. These investigations showed that not only the complex but also the phenantroline molecule itself exerts inhibiting effect, however, the complex is more effective. This phenomenon can be observed during inverse titrations, too.

On summarizing the results of our investigations it can be stated that the features of the induced reaction are not altered in presence of copper(II) ions, only the

Table XVII

| Added substance drop | Taken 0,1 N H ₂ O ₂ | Found ml | Taken K ₂ S ₂ O ₈ 0,1 N ml | Δ H ₂ O ₂ ml |
|---------------------------------|---|----------|---|---|
| Cerimetric titration | | | | |
| — | 10,05 | 6,80 | 10,15 | 3,25 |
| 1 HCl (0,02 N) | 10,05 | 6,98 | 10,15 | 3,07 |
| 1 Ferroin | 10,05 | 7,95 | 10,15 | 2,10 |
| 1 HCl+1 drop Ferroin | 10,05 | 8,10 | 10,15 | 1,95 |
| 1 Phenantroline·HCl | 10,05 | 7,05 | 10,15 | 3,00 |
| 1 Phenantroline·NO ₃ | 10,05 | 7,20 | 10,15 | 2,85 |
| 1 Phenantroline·NO ₃ | 10,05 | 7,15 | 10,15 | 2,90 |
| 1 Phenantroline·NO ₃ | 10,05 | 7,18 | 10,15 | 2,87 |
| Permanganometric titration | | | | |
| 1 Phenantroline·HCl | 10,05 | 6,00 | 10,15 | 4,05 |
| 1 " | 10,05 | 6,03 | 10,15 | 4,02 |
| 1 Phenantroline·NO ₃ | 10,05 | 6,25 | 10,15 | 3,80 |
| 2 HCl (0,02 N) | 10,05 | 6,20 | 10,15 | 3,85 |
| 2 " | 10,05 | 5,95 | 10,15 | 4,10 |
| 2 " | 10,05 | 5,90 | 10,15 | 4,15 |
| | 10,05 | 5,88 | 10,15 | 4,17 |

In presence of 12,73 mg Cu/40 ml

induced error increases considerably, *i. e.* the induced reaction is catalyzed by copper(II) ions. This is not very striking — considering the kinetical nature of the induced reactions — although till now such example cannot be found in the literature. The irreversible oxidation of the ferroin indicator points to that during induced reaction intermediates of very strong oxidizing properties are formed which may destruct partly or wholly the fairly resistant indicator dye.

* * *

Thanks are due to Prof. Dr. Z. G. SZABÓ for his kind interest in this work.

ИНДУКЦИОННЫЕ РЕАКЦИИ СРЕДИ ПЕРОКСИ-СОЕДИНЕНИЙ. III

*Индукционная реакция в системе $\text{H}_2\text{O}_2\text{—H}_2\text{S}_2\text{O}_8\text{—Ce}(\text{SO}_4)_2$
катализируется ионами меди (III).*

Л. Й. Чаньи, Й. Батьяи, Ф. Шольмоши

Действие ионов меди (II) на индукционные реакции в системе



было изучено и показано что свойства индуцированной реакции не были изменены ионами меди (II), они только сильно катализируют индуцированное изменение.

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ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ ОКСИДОВ. VI

Пинаколиновая перегруппировка в кругу 1,3-диолов О внутримолекулярной дегидратации бутандиола-1,3

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В течение изучения химических превращений диолов и органических оксидов поставился вопрос о распространяемости пинаколиновой перегруппировки на 1,3-диолы. Настоящая работа занимается реальной возможностью постановки вопроса, потом путем литературного и экспериментального исследования простого модельного соединения — бутандиола-1,3 доказывает, что пинаколиновая перегруппировка имеет место не только у α -диолов, но она происходит в определенных условиях и у 1,3-диолов. Бутандиол-1,3 превращается на катализаторе Cu-Al между 160—280°C при объемной скорости 0,1—0,5 час⁻¹ с около 75%-ным выходом в метилэтилкетон и с около 10%-ным выходом в масляный альдегид.

1. Введение

Фиштинг [1] обнаружил в 1860 г. в течение исследования реакции пинакона с серной кислотой образование нового вещества, названного им пинаколином. Он не знал строения ни исходного, ни образующегося соединений, следовательно не знал сущности этого процесса. В статье, опубликованной в 1874 г., Бутлеров [2, 3] описал свои исследования, которыми он доказал строения обоих соединений, потом он высказал, что при преобразовании пинакона в пинаколин имеет место внутримолекулярная перегруппировка. По нашему мнению из вышесказанных следует, что открытие пинаколиновой перегруппировки принадлежит Бутлерову. В зависимости от строения исходного 1,2-диола и образующегося карбонильного соединения, идентичная по типу перегруппировка была названа очень часто различными именами — семигидробензоиновая перегруппировка, семипинаколиновая перегруппировка, винильная дегидратация [см. напр. 4, 5, 6, 7].

За время, прошедшее с открытия пинаколиновой перегруппировки, исследователями и исследовательскими группами было доказано путем большой экспериментальной работы, что упомянутый процесс является широко обобщаемой реакцией, т. е. одной из характерных реакции α -диолов. Справочники, занимающиеся пинаколиновой перегруппировкой высказывают единогласно тот же самый взгляд, хотя 1,3-диолы в некоторых условиях — часто при условиях, идентичных с 1,2-диолами — превращаются тоже

в оксо-соединения с тождественным числом углеродных атомов. Относительно этого имелись наблюдения уже в начала столетия, но с тех пор не обратили особого внимания на такой теоретически очень значительный вопрос. Важность его умножается установлениями, приписывающими пинаколиновой перегруппировке огромное значение по Темниковой [6] напр. „самостоятельный интерес” в области α -диолов. Важность и многообразие проблемы наглядно доказывается большим числом публикаций, появившихся в течение считанных с открытия 70—80 лет, которые и в наши дни не доводили проблемы до полного решения, несмотря на то, что в области 1,2-перегруппировок пинаколиновая перегруппировка представляет собой вопрос, которым занимались интенсивнее всего.

Изучая литературу, можно установить, что в области 1,3-диолов и 1,3-перегруппировок тоже имелись попытки для систематизирования рассеянных экспериментальных результатов и для выведения некоторых обобщений [8, 9, 10]. Однако, возможности, предоставленные наличными экспериментальными данными, которые могли бы быть расширены новыми экспериментальными результатами, не были использованы. Нет сомнений в том, что ясному пониманию препятствуют установления, считающие пинаколиновую перегруппировку свойством α -диолов и проповедующие редкость 1,3-перегруппировок, далее установления, которые довольно резко отделяют α -диолы от дисъюнктивных диолов и тем самым пытаются идентифицировать превращения 1,3-диолов больше всего с реакциями 1,4- и 1,5-диолов.

В настоящей работе мы не желаем заниматься всеми внутримолекулярными окислительно-восстановительными превращениями, имеющими место в кругу 1,3-диолов, мы изучаем лишь реакцию бутандиола-1,3 в оксо-соединение. Целью последующих наших исследований является распространение пинаколиновой перегруппировки на целое семейство 1,3-диолов, а также установление экспериментальных условий, которые дают возможность обобщить перегруппировку и в ряде 1,3-диолов. Такие исследования составляют часть нашего плана, состоящего в изучении некоторых — в известном смысле незаслуженно заброшенных — превращений соединений с 1,3-бифункциями, а также в исследовании 1,3-перегруппировок, тоже отнесенных на второй план. Изучение 1,3-перегруппировок может дать до сих пор относительно гетерогенному группированию молекулярных перегруппировок другое освещение и может лежать в основе новой, охватывающей системы.

2. О внутримолекулярном окислении- восстановлении бутандиола-1,3

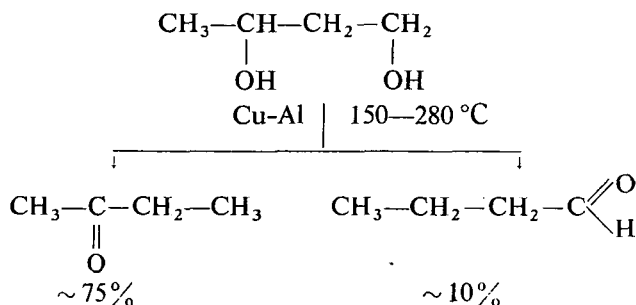
В течение изучения химических реакций диолов мы занимаемся и превращениями, имеющими место под действием дегидратирующих агентов. Мы стараемся найти закономерности между строением диолов, условиями дегидратации и возможными направлениями превращений. Наиболее общим установлением в этом отношении является то, что α -гликоли превращаются при условиях дегидратации вследствие пинаколиновой перегруппировки в карбонильные соединения, дисъюнктивные диолы же образуют окиси или превращаются в диены. Однако, по нашим исследованиям в зависимости

от условий дегидратации главные направления сопровождающих отщепление воды превращений (образование кольцевого эфира, карбонильные соединения, диена, спирта олефинового ряда, а также расщепление молекулы диола на две части) наблюдаются как у α , так и у β , γ и δ -диолов. Задача состоит в том, чтобы — изменяя условия реакций в широком интервале — узнать и общие, и индивидуальные (свойственные) характеристики.

Благодаря потребностям промышленности целый ряд работ занимался изучением бутандиола-1,3 в присутствии дегидратирующих катализаторов. Достиженные результаты резюмируются несколькими монографиями [11—14]. Целью исследований является получение бутадиена-1,3 с возможно большим выходом, исходя из бутандиола-1,3. Для этой цели различные катализаторы типа фосфорной кислоты или фосфата оказываются наиболее пригодными [15—38]. На силикагеле, содержащем окись тантала, бутадиен образуется с хорошим выходом (39).

Превращение бутандиола-1,3 в карбонильное-соединение было впервые наблюдеено *Бауером* и *Каднера* [40—41]. Превращение наблюдалось в присутствии серной кислоты. *Бурнс* и *Николлс* [42] получили на активированном бентоните значительное количество масляного альдегида. В 1952 г. же был опубликован патент, отчитывающийся о том, что при пропускании бутандиола-1,3 над различными оксидными катализаторами образуется метилэтилкетон и кротоновый альдегид [43]. На катализаторе окиси тория-окиси алюминия образуется также метилэтилкетон [44]. Получение бутадиена на фосфатных катализаторах тоже часто сопровождается — хотя в небольшом количестве — образованием вышеупомянутых карбонильных-соединений. Все эти экспериментальные результаты обращают внимание на выведение значительного теоретического заключения, т. е. на то, что внутримолекулярное окисление-восстановление, сопровождающее образование карбонильных-соединений, не является собственностью единственно α -диолов.

Для изучения превращений 1,3-диолов в карбонильные-соединения мы выбрали впервые известное, простое модельное соединение. Исследовали превращение бутандиола-1,3 над катализатором Cu—Al в паровой фазе, в проточной системе, в зависимости температуры и объемной скорости. Температура изменялась между 100—300 °C, а объемная скорость между 0,1—0,5 час⁻¹. Состав образовавшегося продукта исследовался методом газо-жидкостной хроматографии. Главным направлением превращения является — в исследованных условиях независимо от температуры и от объемной скорости — образование метилэтилкетона и масляного альдегида:



В исследованном интервале отношение обоих главных продуктов является тем же самым и суммарное их количество колеблется между 80—85%. Превращение начинается при объемной скорости в $0,1 \text{ час}^{-1}$ между 120—130 °C — в относительно мягких условиях — и между 150—160 °C становится уже полным, даже при более высокой объемной скорости. Процесс сопровождается образованием газообразных продуктов (вероятно пропилена и бутадиена), при более низкой температуре же и возникновением *n*-бутанола и вторичного бутанола. Суммарное количество всех этих побочных продуктов не превышает 25%. Между 160—300 °C для двух изомерных оксо-соединений выход не изменяется. Подводя итоги, можно установить, что в присутствии катализатора Cu-Al бутандиол-1,3 превращается селективно в результате внутримолекулярной дегидратации, и следующего за ней окисления-восстановления в смесь метилэтилкетона и масляного альдегида.

Катализатор, которым мы занимаемся кратко впоследствии, сохраняет активность за очень продолжительное время. На металлических катализаторах процессы происходят вообще с большей селективностью, чем на окисных катализаторах. Например, Юрьев и сотрудники, изучившие дегидратацию триметиленгликоля на катализаторе окиси алюминия [45, 46], наблюдали в катализате образование следующих веществ: пропионового альдегида, акролеина, пропилового спирта, аллилового спирта, дитриметиленгликоля и α -метил- β -этил-акролеина. Применение медного катализатора нашло широкое распространение. Мы встречаем применение разнообразно приготовленных медных катализаторов и при реакциях спиртов, диолов и окисей, например, при гидрированиях [47—50], дегидрированиях [51—53], изомеризационных превращениях [48, 49, 54], а также при дегидратациях [55, 56].

3. О механизме реакции

В области исследования реакции дегидратации диолов α -диолы были изучены интенсивнее всех. Самым характерным направлением реакции является образование карбонильных соединений в результате пинаколиновой перегруппировки. Очень много трудились в этой области Тиффено, Данилов и в последние годы Коллинс с сотрудниками [4, 57, 58, 7]. В случае α -диолов пинаколиновая перегруппировка, имеющая место под действием электрофильных реагентов, — внутримолекулярная нуклеофильная перегруппировка, происходящая через карбониевый ион в качестве промежуточного продукта. Пинаколиновая перегруппировка α -диолов была изучена рядом исследователей и в паровой фазе над различными катализаторами [напр. 4, 59—61]. Механизм происходящих при таких условиях процессов еще не доказано успокоительным образом. Это обстоятельство связано с проблематикой теории гетерогенного катализа, а также с тем, что даже в области механизма процессов, происходящих в жидкой фазе, существуют невыясненные проблемы [6, 7].

При применении различных условий дегидратации, превращение бутандиола-1,3 в карбонильное соединение может быть представлено следующими путями:

- а) Путем внутримолекулярной нуклеофильной перегруппировки через карбониевый ион;
- б) Путем изомеризации непредельных спиртов получающихся в результате дегидратации;
- в) Через β -окись.

При исследовании механизма целесообразно опираться на литературные результаты, т. е. полезно следить за ними с объективной критикой [14, 8, 9, 58, 7, 6, 11, 62, 63, 64, 30, 37, 42, 48, 49, 61, 65, 44]. При изучении 1,3-диолов и спиртов олефинового ряда очень часто предполагается наличие четырехчленного кольцевого эфира в качестве промежуточного продукта [44, 8, 9, 11, 13 и т. д.], для этого, однако, никакого доказательства не существует. Для того, чтобы доказать механизм процесса, нужно проводить опыты для исследования преобразований выше перечисленных возможных промежуточных соединений, имеющих место в идентичных условиях с бутандиолом-1,3. Необходимым оказывается исследовать реакции происходящие при разнообразных условиях, с другими, целесообразно выбранными модельными соединениями. При изучении контактных каталитических процессов необходимо изучать различные теории гетерогенного катализа с точки зрения пинаколиновой перегруппировки.

4. Экспериментальная часть

Бутандиол-1,3. Применяли для исследований препарат технического качества Chemische Werke Huls. Препарат перегоняли предварительно. Т. кип.: 108—110°C (16 рт. мм); n_D^{20} : 1,4394.

Получение катализатора Cu-Al.

К сплаву Cu-Al с размером частиц 3—4 мм, содержащему около 30% меди, прибавляли при охлаждении льдом и при временном осторожном перемешивании столько 16%-ного водного раствора NaOH, чтобы он растворял приблизительно половину алюминия. После подачи щелочи оставляли стоять в течение нескольких часов при комнатной температуре, потом омывали водой, впоследствии дистиллированной водой до достижения нейтральности относительно индикатора фенолфталеина. Сохраняют под водой.

Проведение опытов.

Реакция дегидратации изучалась на приборе, приведенном на рис. 1., где обозначения являются следующими: 1. дозирующий мотор, 2. дозирующий шприц, 3. трубочный реактор, 4. катализатор, 5. термоэлемент, 6. железный кожух, 7. шамотный кожух с нитью накала, 8. теплоизолирующая стеклянная вата, 9. термоэлемент для регулирования температуры, 10, 11. приемники, 12. сосуд Дьюара, 13. счетчик пузырьков, 14. регулятор температуры. Процесс исследовали в трубном реакторе, приготовленном из стекла в непрерывной системе между 100—300°C. Объем пространства ка-

тализатора составляет 50 мл (1,2. П. 11 ~ 50 мл). Температура измерялась термоэлементом железа-константана. Чувствительный пункт термоэлемента помещался в середине реакционной камеры. Бутандиол-1,3 прибавлялся с объемной скоростью 0,1—0,5 час⁻¹. Отдельные опыты проводились с 20 мл вещества и каждый опыт повторялся с целью проверки. Катализат был анализирован без дальнейшей очистки с помощью метода газо-жидкостной хроматографии. Соединенные катализаты ректифицировались на колонке с теоретическим числом тарелок в 20. Физические константы фракций, определенные авторами приведены в таблице I.

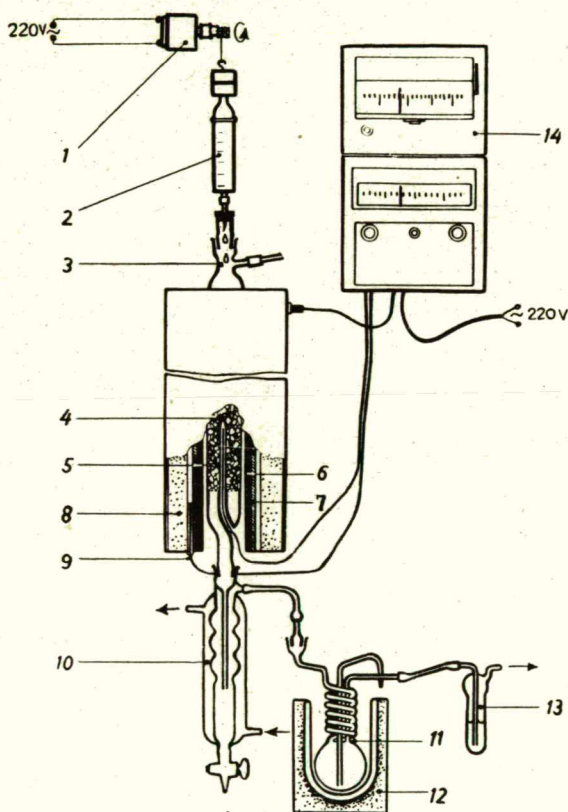


Рис. 1

Определения газовой хроматографией проводили прибором типа *Willy Giede GCHF 18/2* при следующих экспериментальных условиях:

1. Носитель: термолит с размером частиц в 0,2—0,4 мм.
2. Жидкая фаза: диоктилфталат (20%).
3. Колонна: длина: 3 м, внутренний диаметр: 5 мм.
4. Температура: 160 °C.

5. Газ-носитель: водород.
6. Давление: 1 атм. избыточного давления.
7. Детекторный ток: 140 мА.
8. Чувствительность: 2 (конечное отклонение 3,8 мВ).
9. Величина пробы: 0,005—0,01 мл.

На колонне с длиной в 1 м масляный альдегид не отделялся от метил-этилкетона.

Таблица I.

| Полученные продукты | Т. кип. °C | d_4^{20} г/см ³ | n_D^{20} |
|----------------------|------------|------------------------------|------------|
| 1. Масляный альдегид | 75—6 | 0,8171 | 1,3843 |
| 2. Метилэтилкетон | 79—80 | 0,8053 | 1,3790 |
| 3. н-Бутанол | 117—8 | 0,8098 | 1,3993 |
| 4. вт.-Бутанол | 99—100 | 0,8081 | 1,3972 |

UNTERSUCHUNG DER CHEMISCHEN UMSETZUNGEN VON DIOLEN UND CYCLISCHEN ÄETHERN. VI

Pinakolinumlagerung bei 1,3-Diolen. Über die intramolekulare Dehydration von Butandiol-1,3.

M. Bartók und B. Kozma

Im Laufe des Studiums chemischen Umwandlungen von Diolen und Ringäthern tauchte das Problem auf, ob die Pinakolinumlagerung auf 1,3-Diole erstreckt werden kann. Vorliegende Arbeit befaßt sich mit der realen Möglichkeit der Problemstellung, im weiteren — durch die literarische und experimentale Untersuchung der Umwandlung einer einfachen Modellverbindung, des Butandiols-1,3 — wird bewiesen, daß die Pinakolinumlagerung nicht nur eine charakteristische Reaktion der 1,2-Diole darstellt, sondern daß sie auch auf 1,3-Diole erstreckt werden kann. Butandiol-1,3 setzt sich auf Cu—Al Katalysator zwischen 160—280 °C bei der Raumgeschwindigkeit von 0,1—0,5 h mit einer Ausbeute von cca 75% in Methyläthylketon und mit einer Ausbeute von cca 10% in Butyraldehyd um.

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ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ ОКИСЕЙ. VII

Дегидратация 1,4-диолов на скелетных катализаторах

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В области изучения химических превращений диолов и органических окисей настоящая работа занимается внутримолекулярной дегидратацией 1,4-диолов, происходящей на катализаторах скелетного типа (Cu-Al, Pd-Al). Была изучена дегидратация следующих диолов: бутандиол-1,4; пентандиол-1,4; гександиол-2,5; 4-метилпентандиол-1,4; 2,5-диметилгександиол-2,5. Дегидратация была исследована в зависимости от объемной скорости и температуры. Главным направлением превращений между 200—300 °C и при объемной скорости 0,1—0,4 час⁻¹ является образование соответствующих дериватов тетрагидрофурана (80—90%).

1. Введение

В течение изучения химических реакций диолов мы занимаемся и их превращениями, имеющими место при условиях дегидратации. Мы старались найти закономерности между строением диолов, условиями дегидратации и возможными направлениями превращений. Настоящая статья дает отчет о превращении 1,4-диолов на катализаторах скелетного типа. По нашим опытам 1,4-диолы дают при таких условиях γ -окиси с высоким выходом.

В ходе изучения химической литературы может быть установлено, что 1,4-диолы превращаются при условиях и жидкофазной и парофазной дегидратации главным образом в трех главных направлениях: образование гомологов тетрагидрофурана, γ -спиртов олефинового ряда и диенов является самым характерным процессом. Так как настоящая работа изучает образование пятичленных окисей, мы намерены заниматься — разумеется — главным образом первым направлением реакций.

Из способов получения γ -окисей наиболее широко применяется кроме дегидратации 1,4-диолов гидрирование соответствующих гомологов фурана. В некоторых случаях можно пользоваться и изомеризацией γ -спиртов олефинового ряда [1—4]. В области гидрирования фуранового кольца при

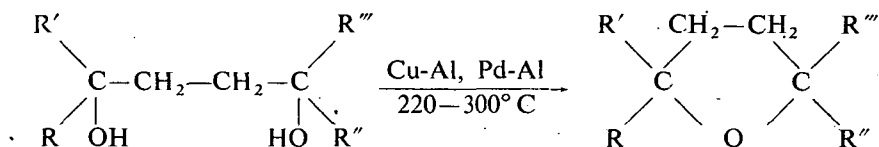
разных условиях обширные исследования были проведены Шуйкиным и сотрудниками.

Благодаря потребностям промышленности дегидратация 1,4-диолов была изучена весьма интенсивно. Достигнутые результаты суммированы и несколькими монографиями [5—8]. Целью исследований является получение бутадиена-1,3 исходя из бутандиола-1,4 с возможно лучшим выходом, [9—22,5].

При дегидратации бутандиола-1,4 применяются главным образом кислые фосфаты, нанесенные на некоторый носитель. Также широко используются различные оксидные катализаторы. Получением тетрагидрофурана, исходящим из бутандиола-1,4, занимаются много работ [5, 18, 23—38]. Многочисленные публикации появились в связи с получением тетрагидрофурана из фурана [напр. 39—42]. Что касается пентандиола-1,4 ученые занимались главным образом жидкофазной дегидратацией его. Таким образом был получен тетрагидросильван [2,5]. *Беати и Маттеи* получили путем паровозной дегидратации в зависимости от качества катализатора тетрагидросильван и пиперилен [43]. α -метилтетрагидрофуран может быть получен с хорошим выходом и путем гидрирования сильвана [44, 45]. Дегидратация гександиола-2,5 была изучена *Реппе* и сотрудниками [5]. Изменяя условия реакции, они получили селективно 2,5-диметилтетрагидрофуран и 2,4-гексадиен. *Рейнольдс, Гиллис* и сотрудники [46, 47] получили из гександиола-2,5 γ -окись с хорошим выходом в жидкой фазе. Упомянутая окись может быть получена также путем гидрирования 2,5-диметилфурана [48, 49] далее путем изомеризации гексен-1-ола-5 [1]. В ходе изучения дегидратации 1,4-диолов, содержащих третичную и первичную гидроксильную группу, *Фаворская* и *Сергиевская* получили 2,2-диметилтетрагидрофуран из 4-метилпентандиола-1,4 а также путем изомеризации соответствующего γ -непредельного спирта. Они исследовали механизм процесса в жидкой фазе. В связи с жидкофазной дегидратацией дитретичных-1,4-диолов тоже появились публикации. Исходя из 2,5-диметилгександиола-2,5 авторы наблюдали в зависимости от условий опытов образование 2,2,5,5-тетраметилтетрагидрофурана, 2,5-диметилгексен-2-ола-5, а также некоторых диенов [4, 5, 37, 47, 50, 51, 52].

2. Экспериментальные результаты и их дискуссия

Чтобы изучать превращение 1,4-диолов, происходящее на скелетных катализаторах, мы исследовали дегидратацию следующих диолов: бутандиол-1,4; пентандиол-1,4; гександиол-2,5; 4-метилпентандиол-1,4; 2,5-диметилгександиол-2,5. Итак, мы занимались внутримолекулярной дегидратацией одного соединения из группы дипервичных, первично-вторичных, дивторичных, первично-третичных и дитретичных 1,4-диолов, происходящей на катализаторах Cu-Al, Pd-Al в паровой фазе в проточной системе, в зависимости от температуры и объемной скорости. Температура изменялась между 200—300°С, а объемная скорость между 0,1—0,4 час⁻¹. Для обнаруживания состава катализата применялся метод газо-жидкостной хроматографии. Главным направлением превращений является при исследованных условиях образование соответствующей пятичленной органической окиси:



где: R, R', R'', R''' = H или CH₃, соответственно вышеперечисленным соединениям.

Выходы колеблются вообще между 80–90% за исключением соединений, содержащих третичную гидроксильную группу, где выход оказывается на 10–20% более низким благодаря образованию соответствующих γ -непредельных спиртов и получающихся в небольшом количестве диенов. При температуре выше 300°C уже начинается, выше 400°C же становится интенсивным вторичное превращение получающихся гомологов тетрагидрофурана, сопровождающее образование диенов и подобных продуктов расщепления. (Более детальным исследованием таких процессов и изучением механизма мы намерены заниматься впоследствии.)

Физические константы примененных в качестве исходного вещества 1,4-диолов и образующихся из последних γ -окисей приведены в табл. I и II.

Оценивая эти результаты, заслуживает отметить факт, что преобразование 1,4-диолов было уже исследовано на медных катализаторах. Такие эксперименты, однако не дали органических окисей, но лактоны [38, 53–56]. При сопоставлении этих результатов с установлениями настоящей работы изменение селективности, вытекающее из различных способов приготовления катализаторов, становится очевидным. В то же время лактоны могут быть получены из 1,4-диолов и на катализаторах типа Ренея [57].

3. Экспериментальная часть

Бутандиол-1,4. Для исследований применялся чистый препарат изделия *Dr. Theodor Schuchardt* (физические константы приведены в табл. I.).

5-гидроксипентанон-2. Был использован чистый препарат советского изделия.

Т. кип.: 85–86°C (10 рт. мм); n_D^{20} : 1,4372.

Пентандиол-1,4. Был получен из 5-гидроксипентанона-2 в автоклаве путем гидрирования на Ni Ренея. Гидрирование проводилось без растворителя при 50°C, под давлением 110 атм.

Гександиол-2,5. Был получен способом, описанным у центандисла, из ацетонилацетона. Выход 80–85%. (физические константы см. в табл. I.)

4-Метилпентандиол-1,4. Был получен из 2-молей 4-гидроксипентанона-2 путем реакции Гриньяра с магнийбромметилом. Выход 65–70%. (физические константы см. в табл. I.)

2,5-Диметилгександиол-2,5. Был получен из 2-молей ацетонилацетона путем реакции Гриньяра с магнийбромметилом. Выход 74%. (физические константы см. в табл. I.)

Катализаторы Cu-Al и Pd-Al приготовились описанным в [60] способом.


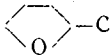
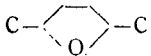
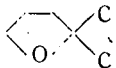
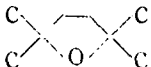
ТАБЛИЦА I

Физические константы 1,4-диолов.

| № | Формула | Т. кип. °C рт. мм | Т. пл. °C | d_4^{20} г/см ³ | $n_D^{t^\circ C}$ | C % | H % | Литература |
|----|---|--|------------------------------|---------------------------------|--|----------------|----------------|-------------------------|
| 1. | $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \qquad \text{OH} \end{array}$ | 230 (790) 106 (0,7) 130-2 (15) | 20,1 | 1,020 1,069 1,0526 | 1,4461 ²⁰ 1,4460 ²⁰ | 53,35 53,15 | 11,18 10,96 | [7] [5] a |
| 2. | $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \qquad \text{OH} \end{array}$ | 125-128 (15) 98,5-99 (1) 125-7 (15) | — | 0,9903 0,9886 | 1,4461 ²⁰ 1,4458 ²⁰ | 57,66 57,62 | 11,61 11,58 | [5] [2] a |
| 3. | $\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \qquad \text{OH} \end{array}$ | 220,8 (760) 132-3 (18) 103-5 (2) 126-8 (15) | — | 0,9618 ²⁰ 0,9625 | 1,4474 ²⁰ 1,4464 ²⁰ 1,4470 ²⁰ | 60,98 61,06 | 11,94 11,84 | [7] [5] [58] a |
| 4. | $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}_3 \\ \qquad \qquad \qquad \qquad \text{CH}_3 \\ \text{OH} \qquad \qquad \qquad \text{OH} \end{array}$ | 124-5 (17) 120-2 (15) | — | 0,9743 0,9733 | 1,4501 ²⁰ 1,4502 ²⁰ | 60,98 60,79 | 11,94 12,08 | [3] a |
| 5. | $\begin{array}{c} \text{H}_3\text{C} \qquad \qquad \text{CH}_3 \\ \diagdown \qquad \diagup \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}_3 \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \qquad \text{OH} \end{array}$ | 117-8 (15) 118-20 (15) | 91 88,9-89 90-92 91 | — | — | 65,70 65,72 | 12,41 12,55 | [5] [4] [52] a |

a данные экспериментальной части

ТАБЛИЦА II
Физические константы γ -оксидов

| № | Формула | Т. кип. °С рт. мм | d_4^{20} г/см ³ | n_D^{20} | С % | Н % | Литература |
|----|---|--|---------------------------------|--|----------------|----------------|-------------------------|
| 1. |  | 62-63 65-67 66-67 (754) | 0,888 0,8886 0,8884 | 1,4043 ²⁰ 1,4065 ²⁰ 1,4063 ²⁰ | 66,63 — | 11,18 — | [38] [5] а |
| 2. |  | 78-79 77-78 78,79 (750) | 0,8484 0,8468 | 1,4040 ²⁰ 1,4046 ²⁰ | 69,72 — | 11,70 — | [5] [2] а |
| 3. |  | 90-92 91,5-92,5 (750) | 0,833 ¹⁷ 0,8290 | 1,4051 ¹⁷ 1,4052 ²⁰ | 71,95 — | 12,08 — | [61] а |
| 4. |  | 90-91 92,2-92,4 (758) 91-92 (754) | 0,8399 0,8441 0,8408 | 1,4058 ²⁰ 1,4045 ²⁰ 1,4055 ²⁰ | 71,95 71,83 | 12,08 12,02 | [3] [59] а |
| 5. |  | 114-117 115,5-116,6 115-119 116-117 (754) | 0,8090 0,8096 | 1,4014 ²⁰ 1,4121 ¹⁸ 1,4012 ²⁰ | 75,00 75,10 | 12,50 12,55 | [5] [4] [52] а |

а — данные экспериментальной части

Проведение экспериментов

Процессы дегидратации проводились тоже описанным в [60] способом. Катализаторы ректификовали на колонке с числом теоретических тарелок 25, потом определяли физические константы чистых веществ. Эти величины приведены в табл. II. В то же время катализаторы анализировали при помощи метода газо-жидкостной хроматографии на аппарате типа *Willy Giede GCHF-18/2* при следующих экспериментальных опытах:

1. Носитель: термолит с размером частиц 0,2—0,4 мм.
2. Жидкость: трикрезилфосфат (20%).
3. Длина колонны: 1 м, внутренний диаметр: 6 мм.
4. Температура: 80° С.
5. Газ-носитель: водород.
6. Давление: избыточное давление 0,2 атм.
7. Детекторный ток: 140 мА.
8. Чувствительность: 2 (конечное отклонение 3,8 мВ).
9. Величина пробы: 0,005—0,01 мл.

UNTERSUCHUNG DER CHEMISCHEN UMSETZUNGEN VON DIOLEN UND CYKLISCHEN AETHERN. VII

Dehydration von 1,4-Diolen auf Katalysatoren von Skelett-Typ

N. I. Schuikin, M. Bartók, R. A. Karahanow, V. M. Schostakowsky

Innerhalb des Studiums der chemischen Reaktionen von Diolen und cyclischen Äthern befaßt sich vorliegende Arbeit mit der auf Katalysatoren von Skelett-Typ (Cu—Al, Pd—Al) vor sich gehenden intramolekularen Dehydration der 1,4-Diole. Es wurde die Dehydration folgender Diole untersucht: Butandiol-1,4; Pentandiol-1,4; Hexandiol-2,5; 4-Methyl-pentandiol-1,4; 2,5-Dimethylhexandiol-2,5. Die Dehydration wurde in der Funktion der Raumgeschwindigkeit und der Temperatur untersucht. Die Hauptrichtung der Umwandlungen zwischen 200—300° C und bei einer Raumgeschwindigkeit von 0,1—0,4 h⁻¹ ist die Bildung der entsprechenden Tetrahydrofuran-derivate.

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A NEW SYSTEM OF MOLECULAR REARRANGEMENTS

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The present classification introduces — beside the generally accepted 1,2-rearrangements — the main group of 1,3-rearrangements including several of the well-known rearrangements (allyl-, CLAISEN-, FRIES-, WÖHLER-, SOMMELET-, FISCHER-HEPP-, ORTON-, HOFFMAN-MARTIUS- *etc.* rearrangements). At the same time the tautomer-changes have also been classified here. The author also gives the classification by subgroups of the more important rearrangement reactions, taking into consideration their generally accepted mechanism in literature.

According to the basic classification of reactions in organic chemistry, besides substitution-, addition- and elimination-processes, the fourth group is given by molecular rearrangements. The systematization of the latter have been undertaken starting from the most diverse points of view [1—7]. In order to throw light to newer processes and their mechanisms we are in need of such a systematization, such a „form”, which is in accordance with the theory of evolution. “Any phenomena of nature and society comes from a certain concrete material *content* and of a corresponding *form*.” As the dialectical interaction of substance and form indicates, the latter always actively affects the former, promotes or hinders its development. New arrangements are generally made necessary by this law of marxist philosophy. By times the collecting of a great number of experimental data, their explanation helped to form such a system, within the frames of which the content — study of the processes and their mechanisms — could develop with a marked speed. The old system proved too tight for further investigations, it was hindering knowledge, a new form became necessary. The conclusions given in the introduction of our earlier paper as well as its experimental results support this statement [8].

By *molecular rearrangement* we understand all the processes, where, as a result of chemical changes, the newly entering ion or radical does not take an identical place with the losing ion or radical. Molecular rearrangements otherwise are called isomerisation reactions. However, in this respect literature does not reflect a uniform standpoint. During *isomerisation* the structure of molecule also changes without the elementary constitution of the molecule being changed. We are of the opinion that the two definitions mean essentially changes of the same structure. The misunderstanding comes so that processes treated by literature as molecular rearrangements are compound in general. However, the essence of the whole change is given by an isomerisation step and we do not consider it reasonable to treat separately, under different designations rearrangements, being theoretically of similar character.

In the present work we have started from the generally accepted WHELAND classification [1] with the only difference that the main group of 1,3-rearrangements is introduced and furthermore, in accordance with some other classifications, even the tautomer changes are regarded as belonging here. We think it superfluous to give an indication of this. The basic idea was given by problems occurring in the study of chemical changes of 1,3 bifunctional compounds. The resolving of these problems likely will lead to the widening of the circle of 1,3-rearrangements.

In essence the classification can be described as follows. The main groups are given by 1,2-, 1,3- and 1,*n*-rearrangements. Within these, according to the mechanism of the processes, there are nucleophyl (N)-, electrophyl (E)-, radical (R)-type, intra (Ia)- or intermolecular (Ir)-rearrangements. Introducing designation letter I (isomerisation), the subgroups can be signed in the following manner:

Table I

| 1,2 | 1,3 | 1, <i>n</i> |
|-----------------------|-----------------------|-------------------------------|
| rearrangement | | |
| 1,2 I _N Ia | 1,3 I _N Ia | 1, <i>n</i> I _N Ia |
| 1,2 I _N Ir | 1,3 I _N Ir | 1, <i>n</i> I _N Ir |
| 1,2 I _E Ia | 1,3 I _E Ia | 1, <i>n</i> I _E Ia |
| 1,2 I _E Ir | 1,3 I _E Ir | 1, <i>n</i> I _E Ir |
| 1,2 I _R Ia | 1,3 I _R Ia | 1, <i>n</i> I _R Ia |
| 1,2 I _R Ir | 1,3 I _R Ir | 1, <i>n</i> I _R Ir |

No systematization can be regarded as a closed, steady one, since it is always subjected to changes with the progress of knowledge. Within the main groups there may occur transitional groups, too. *E. g.* most of the examples of the FRIES-rearrangement can be classified into the group 1,3 I_EIa. At the same time there are cases when the acyl cation migrates into a para-position and the mechanism may be intermolecular.

Today it is yet impossible to give an exact classification of all the known rearrangement reactions. This predisposes first of all a thorough knowledge of the mechanism of the processes and there are complications about this. As to the mechanism of some subgroups of 1,2-rearrangements a general view can be traced in literature. However, the mechanism of 1,3- and 1,*n*-rearrangements, resp., is much more complicated than it can be seen in Table I, since the chain-like 1,2-migrations may occur with less change in the energy as compared to the direct 1,3- and 1,*n*-migrations, resp.

Radical-type isomerisation changes have been dealt with only in the course of the last years. Among them a great number of 1,3-rearrangements are to be found [as *e. g.* 3, 6, 9]. Their mechanism being unclear so far, we disregard to classify them at the present time. Rearrangements on contact catalysts, especially taking place at relatively low temperatures on surfaces with more or less electrons are not rearrangements of the radical type, but they can be treated in a way similar to that of nucleophyl or electrophyl rearrangements.

In this respect first of all we note that a corresponding alteration of the conditions can easily turn a heterolytic isomerisation change into a homolytic one, what considerably enlarges the circle of radical type rearrangements.

In the following we are giving the classification of the more important rearrangement reactions according to the view-points outlined above, taking into consideration their generally accepted mechanism.

1,2 I_NIa: Pinacolin, WAGNER—MEERWEIN-, DEMIANOV-, TIFFENEAU-, BECKMANN-DANILOV-, NAMETKIN-, benzyl-type-rearrangements, CURTIUS-, SCHMIDT-,

LOSSEN- and HOFMANN decompositions, isomerisation of epoxides to oxo-compounds.

- 1,2 I_{Ela}: WITTIG-, STEVENS-, ARBUZOV-rearrangements.
- 1,3 I_{Nla}: Allyl-rearrangement and the rearrangement of 1,3-diols and their derivatives to oxo-compound (mechanism yet unproved).
- 1,3 I_{Nlr}: A less group of tautomer-rearrangements (anionotrop rearrangements).
- 1,3 I_{Ela}: CLAISEN-, FRIES- (the mechanism may be even intermolecular), SOMMELET-, WÖHLER- rearrangements, that of iminoanilines and amidines, N-aryl-sulfamin acids, nitroanilines (the mechanism may be intermolecular, too).
- 1,3 I_{Eir}: Most of tautomer rearrangements (prototrop rearrangements), certain types of the HOFMANN—MARTIUS-rearrangement, FISCHER—HEPP-, ORTON-rearrangements, the rearrangement of alkylanilines.
- 1,n I: This group includes the transannular rearrangements and that of the benzidine. Mention must be made of side reactions directed to para-situation occurring at the 1,3-rearrangements of some aromatic compounds. As the group of 1,n-rearrangements is increasing and the mechanisms are more and more thoroughly understood, in the future it seems possible to form more main groups.

The importance of this new classification may be sought in the following:

1. It gives a better arrangement of the numerous experimental data.
2. Promotes to solve the doubtful problems.
3. Gives rise to newer questions.

This new classification of molecular rearrangements is in its present form only a preliminary communication. The characteristics of the main- and sub-groups, their mechanisms, the collected data in literature and their discussion together with experimental results will be published later.

НОВАЯ СИСТЕМА МОЛЕКУЛЯРНЫХ ПЕРЕГРУППИРОВОК

М. Барток

В новой систематизации автором была принята — кроме общепринятых 1,2-перегруппировок группа 1,3-перегруппировки, к которой принадлежат несколько из известных перегруппировок как напр. аллильное-перераспределение, перегруппировка Клайзена, Фриза, Велера, Сомелета, Фишера-Геппа, Ортона, Гофман-Марциуса и т. д. В то же время таутомерные перегруппировки были также приняты как 1,3-перегруппировки. В настоящей работе дается подгруппировка важнейших реакций перегруппировки — именуя в виду их общезвестный по литературным данным механизм.

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SYNTHESIS OF SUBSTANCES EFFECTING ON C.N.S. IV*

Synthesis and Pharmacological Examination of Some Aminoethers

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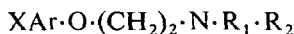
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Some $R \cdot O \cdot (CH_2)_2 \cdot N \cdot R_1 \cdot R_2$ type of amino alkylethylether derivatives where the R -radical were phenyl or substituted phenyl or naphthoyl-radical, while the $N \cdot R_1 \cdot R_2$ meant diethylamino-pirolidino-, morpholino-, piperidino-radical were prepared with routine techniques. A few quaternary derivatives have been also prepared from this compounds. Examining the pharmacological activities the tertiary compounds showed antiadrenaltic activity, among the quaternary derivatives however, highly active ganglioplegic compound could be noted.

Previously the correlation of pharmacological effect and chemical structure was treated concerning the different substituted carbonic ester [1–3], tertiary aminoaryl-propene and propane [4], aryl-aminothioether and sufoxide [5], acidamides [6] etc. Some drugs had been selected from these groups and their pharmacological introduction is under way (*Gedeon Richter Pharmacological Works, Budapest*). The antiadrenaline effect of the aminoethylphenylethers [7], "as well known" has been earlier examined. The aim of our earlier examinations was to see, the effect of the exchange in the ether oxygen to sulphur causes [5]. It was noted that the tertiary amino-ethyl-aryl-thioethers become adrenaline mobilisers and ganglion excitators. So this isoster exchange proves a significant change of pharmacological properties. The first effective and in the medical practice still used aminoether derivatives was produced by FOURNEAU [7]. Later investigating systematically this group numerous compounds were demonstrated possessing antihistamine and nicotine-like effect. [7, 8] Efforts were made to contribute to some new details to the problem.

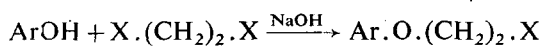
The general formulae of the compounds synthesized:



The synthesis of this group could be realized merely in several steps. The synthesis of halogen ethylaryl-ethers started from phenols was determined by WOHL and BERTHOLD [9] with dihalogenethane and the halogen-ethylarylether obtained could

* Previously entitled: An Investigation of the Connection between Physiological Activity and Chemical Structure of New Drugs Acting on the Central Nervous System. (Central Nervous System = C. N. S.)

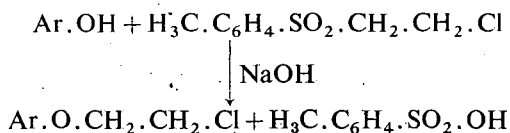
be connected with various secondary basis and so the above mentioned group can be reached.



X = halogen atom

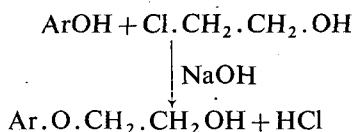
The disadvantage of this synthesis is that it may easily result diarylethylether.

However with PERKIN's [10] method the chlorethyl-group yields better results with alcohols and phenols. In this method β -chlorethyl-p-toluene-sulfonic acidesters are employed for the intake of the chlorethyl-group:

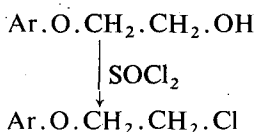


The method is mainly used to prepare naphthoyl ethers.

KIRNER [11] synthesized the β -chlorethyl-phenolethers in two steps. The phenyl-ethanol-ether is formed first at the reaction taking place between the phenol and ethylenechlorhydrine in alkalic solution:

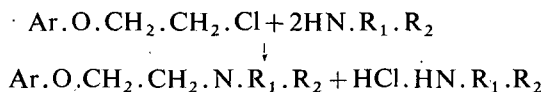


which can be transformed into β -chlorethylphenyl-ether with thionyl-chloride:

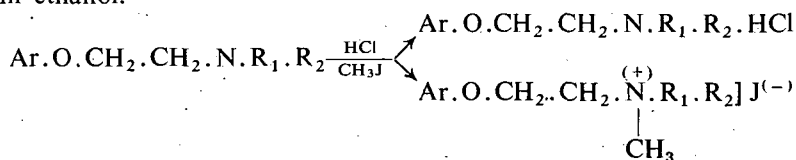


Aryl-thioether may be also obtained with this method [12].

The halogenethylphenyl-ether was reacted, with the excess of secondary amines (piperidine, pirrolidine, morpholine, ethylamine) in dry pyridine.



After having the hydrochlorides of the above mentioned substances reacted with calculated amount of alcoholic hydrochloric acid and the methiodides with methyl-iodide in ethanol.



Experimental *β -hydroxyethylphenyl-ether (11)*

17 gr of NaOH is solved in 20 ml of water and added to 30 gr of phenol. It is heated in water-bath and 24,4 gr ethylenechlorohydrine is added slowly stirring and constantly heating it for 10 minutes, than cool it. It results two phases, the water phase is separated from the oil and extracted with ether. Combine the upper phase and the ether extracts, washed 3—4 times with 20 ml of water and the etheric solution is dried (Na_2SO_4). After a while the solvent is distilled, the residue is fractionated.

Bp.: 128—130 °C/20 mm.

Yield: 84%.

 β -chloroethyl-phenylether (11)

30 gr of pyridine is added to 35 gr of β -hydroxyethyl-phenylether and slowly dropwise 30 ml of fresh distilled thionylchloride added (in the case of rapid reaction is cooled in ice), heat it in water bath for a short while thereafter cool it then pour it into ice cold water whereupon the product is crystallized. After filtering it is washed with water, diluted NaHCO_3 solution and is solved in ether. The ether is dried (Na_2SO_4), filtered and finally distilled. The oil-like residue is fractionated.

Bp.: 217—220 °C.

Bp.: 122—123 °C/26 mm.

Mp.: 27—28 °C.

Yield: 88%.

 β -bromoethylphenyl-ether (9)

14 gr of phenol is mixed with 15 ml of dibromoethane and 50 ml of water is added to it. Refluxed for a time in oil-bath at 100—105 °C constantly stirring it. 4 ml (4 N) of NaOH solution is slowly dropped into it. Filtering it in hot condition and let it cool. Two layers are formed following the cooling. The oil-layer is separated and the aqueous part is repeatedly extracted with ether. The oil-phase and the ether extract are combined washed with diluted NaOH. Drying (Na_2SO_4), the filtrate distilled and the residue is fractionated.

Bp.: 114—117 °C/10 mm.

Yield: 59%.

 β -chloroethylphenylether (10)

38 gr of phenol, 17 gr of NaOH solved in 30 ml of water adding to this 94 gr of β -chloroethyl-p-toluenesulfuric acidester is heated in water bath for 2—3 hours constantly stirring. Turning it into basic with potash following steam distillation it an agreeable smelling distillate is obtained. (During the steam-distillation 1—2 gr of diphenylethylen ether is formed in the cooler.) The oil has been separated, dried (Na_2SO_4) and fractionated.

Bp.: 217—220 °C.

Yield: 90%.

 β -bromoethyl-naphthoylether (9)

4 gr of NaOH solved in 50 ml of water is added to 21,6 gr of β -naphthol and 28,2 gr of dibromomethane. Stirring it for 24 hours and keeping it refluxed in

oil-bath at 100–110 °C. After cooling two layers are separated. The water phase is extracted as above. The oil phase and the ether extract are combined, dried (Na_2SO_4) and the ether evaporates, the residue is recrystallized from alcohol.

Mp.: 96 °C.

Yield: 40%.

N-piperidino-ethylphenyl-ether

17,03 gr (0,2 M) of piperidine is added to 15,66 gr (0,1 M) of β -chloroethyl-phenylether and reflux it in oil-bath at 150 °C for 30 minutes. Piperidine–HCl is precipitated then filter it, wash with dry benzene. The benzene as well as the unreacted piperidine are distilled and the residue is fractionated in vacuum. (Tabl. II and III show the bp., physical constants and analysis of compounds).

N-pirrolidino-ethylphenylether

14,22 gr (0,2 M) of pirrolidine was added to 15,66 gr (0,1 M) of β -chloroethyl-phenyl-ether. It was refluxed in oil bath at 140 °C for 1 hour. It results a jelly-like precipitate of pirrolidine-HCl. The pirrolidine-HCl and the unreacted pirrolidine is washed with water as well as diluted potash. The fluid is three times extracted with ether, dried (Na_2SO_4), then the solvent is evaporated. The residue is fractionated. (Tabl. II and III).

N-morpholinoethylphenyl-ether

17,43 gr (0,2 M) of morpholine is added to 15,66 gr (0,1 M) of β -chloroethyl-phenyl ether. Keeping refluxed in oil-bath at 170–175 °C for 1 hour. After cooling morpholine-HCl crystals are precipitated filter it and washed with dry benzene. The residue after evaporation is fractionated. (Tabl. II and III).

N-diethylaminoethyl-phenylether

21,74 gr (0,3 M) of diethylamine is added to 15,66 gr (0,1 M) of β -chloroethyl-phenylether. It is refluxed in oil-bath at 150 °C for 3–4 hours. The rest of the procedure is followed as above (Tabl. II and III).

2,4-dichlorophenyl- β -hydroxy-ethylether

82 gr of 2,4-dichlorophenol is solved in 200 gr 10% of NaOH and add 47 gr of ethylenechlorohydrine refluxed it for 12 hours. After cooling it is extracted with ether and the extract is washed with 5% NaOH solution. The ether is evaporated and the oil like residue is fractionated.

Bp.: 158–160 °C/11 mm.

Mp.: 57–58 °C.

Yield: 42,8%.

2,4-dichlorophenyl- β -chloroethylether

46 gr of PCl_5 is added to 44,5 gr of 2,4-dichlorophenyl- β -hydroxyphenyl-ether and heated over asbestos. The reaction rapidly occurs. The by-product is distilled and oil-like residue is fractionated.

Bp.: 126–127 °C/8 mm.

Yield: 63,58%.

2,4-dichlorophenyl- β -bromo-ethylether. (13)

326 gr (2 M) of 2,4-dichlorophenol, 470 gr of dibromoethane and 1 l of distilled water are put in a 3-necked flask of 3 l content. It is refluxed with constant stirring while 8 gr (2,1 M) of NaOH solution is being added for 1 hour. After cooling the two phases are separated and the upper one is washed, dried (Na_2SO_4), filtered and fractionated.

Bp.: 157—159 °C/10 mm.

Yield: 69%.

N-piperidino-ethyl-2,4-dichlorophenylether

10 gr of β -bromoethyl-2,4-dichlorophenylether is added to 6,7 gr of piperidine solved in 20 ml of dry benzene and refluxed 50 minutes. After cooling is filtered and washed with benzene. The solvent is distilled and the oily residue is fractionated. (Tabl. II and III).

N-diethylaminoethyl-2,4-dichlorophenylether

9,5 gr of diethylamine is added to 15 gr of β -bromoethyl-2,4-dichlorophenylether and refluxed at 150 °C for 3 hours. After cooling it is filtered, the precipitate is washed with benzene. The solvent is distilled and from the residue results in hydrochloride with alcoholic HCl.

p-toluene sulfonic acid chloride is prepared with the method described by VOGEL. [14].

 *β -chloroethyl-*p*-toluene sulfonic acidester (10)*

95 gr of *p*-toluenesulfonic acidchloride with 100 gr of ethylenechlorohydrine is refluxed 155—160 °C (HCl gas is formed) for about 2—3 hours. The excess of ethylenechlorohydrine is distilled (over 60 gr) in vacuum. The residue is alkalized with diluted excess of NaOH and extracted with benzene. The combined extract is dried (K_2CO_3), filtered and distilled. The residue is fractionated.

Bp.: 210 °C/21 mm.

Bp.: 155—157 °C/3 mm.

Yield: 87%.

 β -chloroethyl- β -naphthylether (10)

8 gr of NaOH and 47 gr of β -chloroethyl *p*-toluene sulfonic acid ester sold in 14 ml of water are added to 30 gr of β -naphthol. It is stirred and heated in steam-bath for 1 hour. The product is solidified while cooled, then ground and dried in an exsiccator over potash. The by-product β -naphthylether can be separated by petroleum ether extraction. Having concentrated the petroleum ether extract the expected material is crystallized in plate forms.

Mp.: 83 °C.

Yield: 75%.

β -chloroethyl α -naphthyl-ether. (10)

It is produced like the β -chloroethyl- β -naphthylether.

Mp.: 28 °C.

Bp.: 202 °C/16 mm.

Bp.: 172—175 °C/3 mm.

Yield: 51%.

 β -piperidinoethyl- α -naphthylether

17,03 gr (0,2 M) of piperidine is added to 20,67 gr (0,1 M) of β -chloroethyl- α -naphthylether. It is kept at 150—160 °C for 1 hour. The precipitate is filtered, washed with benzene and dried (Na_2SO_4). The solvent is distilled and the residue is fractionated.

(Tabl. II and III).

 β -pirrolidinoethyl- α -naphthylether

14,22 gr (0,2 M) of pirrolidine is added to 20,67 gr (0,1 M) of β -chloroethyl- α -naphthylether. Refluxed at 140 °C for 2 hours. After cooling the precipitate is filtered, washed with benzene and the solvent evaporated and the residue is fractionated (Tabl. II and III).

 β -piperidinoethyl- β -naphthylether

20,67 gr (0,1 M) of β -chloroethyl- β -naphthylether is solved in 17,03 gr (0,2 M) of piperidine. The solution is kept in oil bath at 150 °C for 0,5 hour. After cooling a praecipitate is obtained, it is filtered and washed with benzene. The solvent is distilled and the residue is fractionated. (Tabl. II and III).

 β -pirrolidino-ethyl- β -naphthylether

It was produced similarly to the afore said method.

Preparation of hydrochlorides

The basis is solved in absolute ethanol or ether and reacted with calculated amount of ethanolic and etheric hydrochloric acid.

Preparation of methiodides

The basis is solved in abs. ethanol and reacted with the calculated amount of methyl iodide.

Keeping it for a couple of days at room temperature the quaterner compounds are precipitated. Filtered it and recrystallized from dry ethanol.

They are light sensitive.

* * *

The authors wish to express their thanks to J. FÜLÖP, technician, for the analyses carried out in the Analytical Section of our Institute as well as to *Gedeon Richter Pharmaceutical Works, Budapest* for their kind support.

Table I (Pharmacological effect)

| Basis | Tertiary (HCl) | Quaternary methiodide |
|---|-------------------------------|-------------------------------|
| $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | antiadrenalinic effect (100) | slight ganglion excitator |
| $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_8$ | antiadrenalinic effect (50) | — |
| $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_8 \cdot O$ | antiadrenalinic effect (10) | somewhat nicotine-like effect |
| $C_6H_3Cl_2 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | antiadrenalinic effect (20) | slight ganglioplegic |
| $C_6H_3 \cdot Cl_2 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_{10}$ | antiadrenalinic effect (30) | — |
| $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_{10}$ | antiadrenalinic effect (100) | — |
| $\alpha\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | slight antiadrenalinic effect | slight ganglioplegic |
| $\alpha\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_8$ | adrenaline mobilizer | slight ganglioplegic |
| $\beta\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | no effect on adrenaline | strong ganglioplegic (3×TEA) |
| $\beta\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_8$ | no effect on adrenaline | ganglioplegic (1×TEA) |
| $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10} \cdot J$ (+) (−) CH ₂ C ₆ H ₅ | — | strong ganglioplegic (3×TEA) |

Table III

| Number | Tertiary hydrochloride | | | | | | | | |
|--------|------------------------|--------------|------|------|-------|---------|------|------|-------|
| | Mp. °C | Calculated % | | | | Found % | | | |
| | | C | H | N | Cl(−) | C | H | N | Cl(−) |
| 1 | 175 | 64,67 | 8,38 | 5,79 | 14,67 | 64,75 | 8,32 | 5,67 | 14,49 |
| 2 | 154 | 50,27 | 7,97 | 6,15 | 15,57 | 50,13 | 7,88 | 5,94 | 15,39 |
| 3 | 189 | 59,13 | 7,03 | 5,75 | 14,55 | 59,27 | 7,20 | 5,62 | 14,47 |
| 4 | 145 | 62,72 | 8,82 | 6,10 | 15,43 | 62,50 | 8,77 | 6,05 | 15,30 |
| 5 | 172 | 50,04 | 5,85 | 4,51 | 11,32 | 50,25 | 5,93 | 4,70 | 11,20 |
| 6 | 134 | 48,40 | 6,07 | 4,96 | 12,00 | 48,72 | 6,21 | 4,79 | 12,31 |
| 7 | 175 | 61,60 | 7,62 | 4,79 | 12,12 | 61,45 | 7,63 | 4,77 | 12,10 |
| 8 | 152 | 69,17 | 7,26 | 5,04 | 12,76 | 69,38 | 7,20 | 5,03 | 12,65 |
| 9 | 209 | 61,60 | 7,62 | 4,79 | 12,12 | 61,62 | 7,55 | 4,81 | 12,02 |
| 10 | 208 | 69,17 | 7,26 | 5,04 | 12,76 | 69,40 | 7,15 | 5,00 | 12,70 |

Table II

| Number | Basis | Summary form | Mol. wt. | Bp. °C/Hgmm | n_D^t | Yield |
|--------|--|----------------------|----------|----------------|----------------------|-------|
| 1. | $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | $C_{13}H_{19}ON$ | 205,29 | 131/1 | 1,5280 ²⁵ | 75 |
| 2. | $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_8$ | $C_{12}H_{17}ON$ | 191,27 | 114/1 | 1,5270 ²⁵ | 68 |
| 3. | $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_8 \cdot O$ | $C_{12}H_{17}O_2N$ | 207,26 | 146/4 | 1,5320 ²⁵ | 73 |
| 4. | $C_6H_5 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_{10}$ | $C_{12}H_{19}ON$ | 193,29 | 131/5 | — | 32 |
| 5. | $C_6H_5 \cdot Cl_2 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | $C_{13}H_{17}ONCl_2$ | 274,14 | 146/2,5 | — | 62 |
| 6. | $C_6H_5 \cdot Cl_2 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_{10}$ | $C_{12}H_{17}ONCl_2$ | 262,19 | — | — | — |
| 7. | $\alpha\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | $C_{17}H_{21}ON$ | 255,35 | 120/2—3 | — | 52 |
| 8. | $\alpha\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_8$ | $C_{16}H_{19}ON$ | 241,32 | 116/3 | — | 48 |
| 9. | $\beta\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_5H_{10}$ | $C_{17}H_{21}ON$ | 255,35 | 150—160/3—4 | — | 51 |
| 10. | $\beta\text{-}C_{10}H_7 \cdot O \cdot (CH_2)_2 \cdot N \cdot C_4H_{10}$ | $C_{16}H_{19}ON$ | 241,32 | 140—145/3 | — | 51 |

(continued)

| Number | Quaternary methiodide | | | | | | | | |
|--------|-----------------------|--------------|------|------|-------|---------|------|------|-------|
| | Mp. °C | Calculated % | | | | Found % | | | |
| | | C | H | N | J(—) | C | H | N | J(—) |
| 1 | 130 | 48,45 | 6,39 | 4,03 | 36,54 | 48,72 | 6,25 | 4,02 | 36,17 |
| 2 | — | — | — | — | — | — | — | — | — |
| 3 | 105 | 44,70 | 5,80 | 4,01 | 36,33 | 44,87 | 5,85 | 4,22 | 36,01 |
| 4 | — | — | — | — | — | — | — | — | — |
| 5 | 165 | — | — | — | 31,92 | — | — | — | 31,40 |
| 6 | — | — | — | — | — | — | — | — | — |
| 7 | 132 | 54,42 | 6,09 | 3,53 | 31,95 | 54,70 | 6,00 | 3,39 | 31,62 |
| 8 | 125 | 53,27 | 5,79 | 3,66 | 33,11 | 53,22 | 5,77 | 3,58 | 32,89 |
| 9 | 152 | 54,42 | 6,09 | 3,58 | 31,95 | 54,67 | 6,23 | 3,47 | 31,55 |
| 10 | 124 | 53,27 | 5,79 | 3,66 | 33,11 | 53,22 | 5,66 | 3,62 | 32,97 |

ИЗУЧЕНИЕ ДЕЙСТВИЯ МЕЖДУ ФИЗИОЛОГИЧЕСКИМИ И ХИМИЧЕСКИМИ СТРОЕНИЯМИ ВЕЩЕСТВ, ДЕЙСТВУЮЩИХ НА ЦЕНТРАЛЬНЫЙ НЕРВНЫЙ МОЗГ. IV

Синтез терциераминовых ациламидов

Ш. Фельдеак, Й. Цомдош, Б. Маткович и Й. Порсас

Уже известными способами была изготовлена несколько $P \cdot O \cdot (CH_2)_2$, IP_1P_2 , производных типа аминовалкил — этилового эфира, где радикал P являлся замещённым фениловым нафтиловым радикалом. IP_1P_2 = Диетиламино- пиперидино-, пи-пеолидино-, или морфолиновым основаниям.

Из этих соединений было изготовлено несколько квагернерных производных. Рассматривая их фармакологическую активность, установилось, что терциерные соединения обладали активностью антиадреналина. Между кватерническими производными же встречались очень активные блокирующие ганглиона.

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SYNTHESIS OF SUBSTANCES EFFECTING ON C.N.S. VI
Synthesis and Previous Pharmacological Examinations of Ketoxime
Isomer—Pairs

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During our earlier synthetic examinations efforts have been made to separate some syn- and anti-isomers of piperidine-ketoximes. This paper presents the separation of ketoxime-isomers and their informing pharmacological investigations.

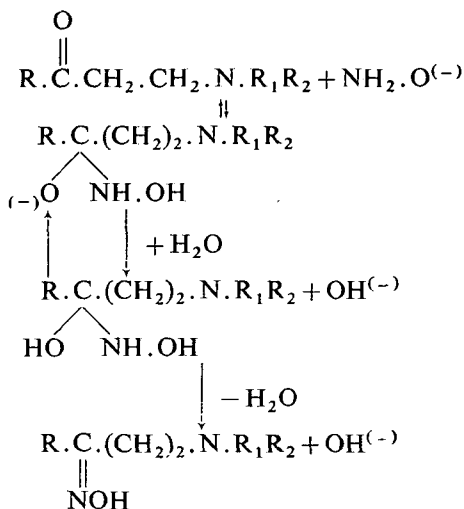
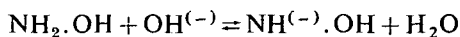
Generally in the literature, of the aldoxime and ketoxime isomers is described either alone the more stabile or the mixture of the syn- and anti-oximes.

VARGHA, OCSKAY [1, 2] treated the production and separation of the various furyl-ketoxime-pairs and the determination of their configuration. The general and the above mentioned authors' experience is in most of the cases the m. p. of anti-isomer is higher that is the most stabile form and the syn-isomer can be produced from the anti-isomer with dry etheric-HCl or with HCl-gas. These authors could demonstrate differences also in the UV-spectrum of the ketoxime-isomer-pairs [1].

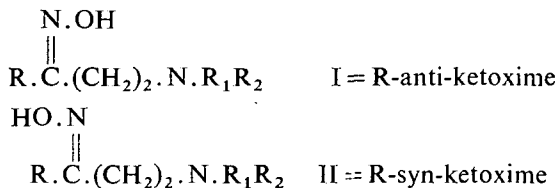
Several γ -aminoketones were prepared to the synthesis of *p*-alkyl-aryl-propene-derivatives [3] and so in many cases there was a possibility to prepare the oxime isomer pairs. FOULHOUX [4] observed that the monozonitroso-acetone possesses strong antinicotinic activity [4]. So in the case of some amino-ketones oxime-isomer pairs were prepared in order to be able to examine the eventual difference observable between their pharmacological activity and to connect it with the chemical structure.

Our further aim is to prepare to investigate the complex-forming properties of oxime isomers and to reveal its UV-spectrum further to synthesize their various derivatives such as acetate and tosylate, *etc.*

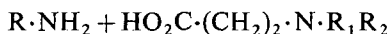
The ketoximes where prepared in alkalic conditions when taking into consideration the mechanism suggested by INGOLD [5].



I and II isomer pairs are existing:



When I and II subjected to BECKMANN-rearrangement and hydrolysis the following derivatives can be expected in I:

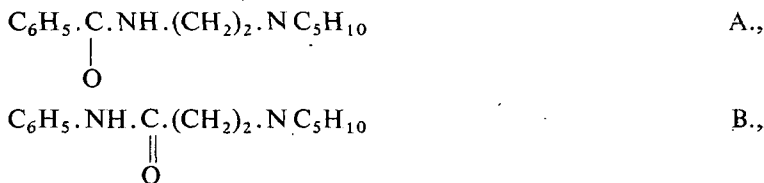


whereas in II:



as it is generally known in BECKMANN-rearrangement always the group in the anti-position is shifted.

Carrying out SCHMIDT reaction the following two products (A, B) were obtained in the case of 1-piperidino-3-phenyl-propanone-3 examined [6] and produced also by us



Having hydrolysed the substances A, B we obtained the designated products.

The structure of syn- and anti-oxime isomers can, be studied with FÖLDI's complex forming method [7].

We could demonstrate a difference in pharmacological activity between the two 1-piperidino-3-phenyl-propanone-3-oxim-isomers, inasmuch as the anti-isomer of a higher m. p. showed in a smaller dose a higher antinicotinic activity than the syn-pair.

Experimental:

1-piperidino-3-phenyl-propanon-3-(I).

Substance I was obtained from piperidine-HCl, paraformaldehyde and acetophenone with Mannich-condensation. [8].

1-piperidino-3-phenyl-propanone-oxime-3-HCl (II, III).

It was produced with different methods and in spite of different circumstances always obtained, the presumable R-anti-oxime with the higher m. p. (II).

Two typical examples:

20% hydroxylamine-HCl excess later $\text{NH}_2\text{OH}\cdot\text{HCl}$ is added to the 100 ml ethanol solution of 15,3 g I. and refluxed in water bath for 3 hours. Then filter it hot and evaporate the alcohol at atmospherical pressure and dry with benzene ethanol azeotrop. Dissolving the substance in abs. acetone 12 g of crystalline substance is obtained.

M. p.: 89—90 °C.

The substance is extremely hygroscopic.

It can be well solved in benzene, methanol, ethanol and butanol; while in acetone very poorly, if cold it is not solving in ether and ethylate all, heated it slowly solves in latter two cases. Recrystallized from ethanol, acetone (1:2) mixture an other product is separated its m. p. 177 °C.

This is likely the R-anti-modification (II). Solving substance II in dry MeOH streaming it HCl-gas with cooling (9) quantitatively a substance of lower m. p. is produced.

M. p.: 128—130 °C.

Presumably this will be an other isomer (R-syn modification) III. The analysis of both substances is in good agreement with the oxime-hydrochlorides (Tabl. I).

(The physico-chemical and analytical data of the substances are shown in Table I.)

The oxime is prepared with an other method with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NaHCO_3 in aqueous MeOH: 5 g substance I is solved in 50 ml of MeOH and adding the solution of 2,2 g NaHCO_3 in 15 ml of distilled water and 1,8 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$. Refluxed it in water bath for 2 hours and after distilled the solvent. The residue is suspended in water and extract it with ether. Drying (Na_2SO_4 sicc.), filtering and evaporating, small white crystals are obtained.

M. p.: 107—109 °C, presumably it is a mixture of two isomers, which during the recrystallization becomes the stable isomer (II).

After streaming dry HCl gas through its solution can be turned substance III, too.

Table I

| Name of the substances | Summary form | M. w. | Physical data | ANALYSIS | | | | | | | |
|--|--------------|-------|-----------------|------------|------|-------|-------|-------|------|-------|-------|
| | | | | Calculated | | | | Found | | | |
| | | | | C | H | N | Cl | C | H | N | Cl |
| α -1-piperidino-3-phenylpropanone-3-oxime | HCl | 263 | mp.: 177 °C | 68,87 | 9,64 | 10,65 | 13,31 | 68,7 | 9,60 | 10,47 | 13,2 |
| β -1-piperidino-3-phenylpropanone-3-oxime | HCl | 263 | mp.: 128—130 °C | 68,87 | 9,64 | 10,65 | 13,31 | 68,80 | 9,47 | 10,80 | 13,6 |
| α -1-piperidino-acetophenoneoxime | HCl | 249 | mp.: 136 °C | 62,6 | 5,62 | 11,24 | 10,04 | 62,6 | 5,2 | 11,0 | 9,6 |
| β -1-piperidino-acetophenoneoxime | HCl | 249 | mp.: 118—120 °C | 62,6 | 5,62 | 11,24 | 10,04 | 62,4 | 5,4 | 11,6 | 9,8 |
| α -1-N-piperidino-butanone-3-oxime | HCl | 206 | mp.: 194—198 °C | 52,4 | 9,23 | 13,6 | 17,0 | 51,65 | 9,32 | 13,70 | 17,20 |
| β -1-N-piperidino-butanone-3-oxime | HCl | 206 | mp.: 150—152 °C | 52,4 | 9,23 | 13,6 | 17,0 | 51,95 | 9,2 | 13,72 | 17,30 |

ω -piperidino-acetophenone (IV) (10).

Substance IV was obtained by condensing ω -bromo-acetophenone and piperidine.

ω -piperidino-acetophenone-oxime (V, VI) (11).

Oxime V was prepared from HCl of substance IV.

M. p.: 118—120 °C.

Solving oxime V in abs. MeOH and bubbling dry HCl-gas through the solution the HCl salt of the other oxime-isomer is obtained (VI).

M. p.: 190 °C.

The m. p. of oxime-VI 135—137 °C (11), which can be obtained by fractionated crystallization of isomer V from MeOH.

1-N-piperidino-3-butanone (VII) (12).

It was prepared from piperidine-HCl, paraformaldehyde and acetone.

1-N-piperidino-3-butanone-oxime (VIII).

10 g of ketone (VII) is solved in 35 ml of abs. EtOH and 4,5 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 5,47 g dry NaOAc is added to it. Refluxed in water bath for 5 hours. The hot solution is filtered. Evaporated it white precipitate occurs m. p.: 165—170 °C. Recrystallized from MeOH m. p.: 150—152 °C. (Table I.)

* * *

We wish to express our thanks to Gedeon Richter Phar-

maceutical Works, Budapest, for the substances, for the analyses to our Analytical Laboratory, and to Miss L. NAGY, chemist and to J. FÜLÖP, laboratory technician, for their valuable assistance.

ИЗУЧЕНИЕ ДЕЙСТВИЯ МЕЖДУ ФИЗИОЛОГИЧЕСКИМИ И ХИМИЧЕСКИМИ СРОЕНИЯМИ ВЕЩЕСТВ, ДЕЙСТВУЮЩИХ НА ЦЕНТРАЛЬНЫЙ НЕРВНЫЙ МОЗГ. VI

Синтез измерных пар кетоксима и их фармакологическое рассмотрение

Б. Маткович, Ш. Фельдеак, Ж. Тедеи, И. Чех, Й. Порчас.

Уже раньше удалось приготовить изомерную пару многих пиперидин-кетоксима. Публикация занимается изготовлением изомеров кетоксима и их предварительными фармакологическими рассмотрениями.

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SYNTHESIS OF SUBSTANCES EFFECTING ON C.N.S. VII

The Synthesis of the Tertiary Aminoacetyl and Propionyl Derivatives of Aromatic and Homocyclic Amines

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(Received June 15, 1963)

It was known from our earlier publications that acidamide derivatives possess depressing effect on C.N.S. [1, 2].

Accordingly systematic examinations were carried out in the group of acidamides concerning the correlation between the effect and structure.

The present paper treats primarily the condensation of naphtylamines and homocyclic amines with chlorcarbonic acid chlorides (chlor-acetic acid chloride and chlor-propionic acid chloride) and the obtained aromatic or homocyclic amino-acid haloids were reacted with secondary amines. Having prepared series it became possible to determine the influence of the distance and the different bases on the C.N.S. effect.

Several local anaesthetic, antinicotine active compounds were found among synthesized series.

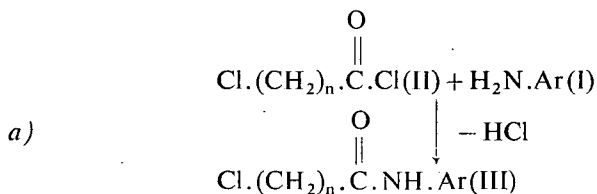
The compounds condensed with morpholine had in general neither C.N.S. nor local anaesthetic effect except in very high concentration.

In the III. part (1) of our publication was summarized the question what kind of structure is needed for an acidamide to exert an effect on CNS. At any rate numerous well known drugs have acidamide structure.

Having produced acid amides with MANNICH-condensation we looked for an other way to synthesize new acidamide derivatives.

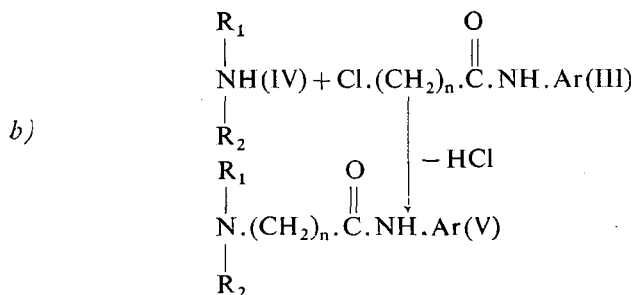
Using in our experiments aromatic or homocyclic amines (I) we finally obtained chloroalkyl-acid amides (III) due to different reactivity of the two halogens of the chloro-carbonic acid chlorides (II) which we used for further reactions.

The reaction of chloro-carbonic acid chloride with primary amine occurs as follows:



This reaction was used to synthesize, among others, β -chloropropionic acid-N-anilide as starting material of hydro-carbostyryle (3).

The produced chloro-carbonic acid-aryl or homocyclic amines (III) could be reacted with different secondary amines (IV) and so the end product of the synthesis is reached (V)



For the condensation of B were primarily employed piperidine, pyrrolidine and morpholine.

The process of the synthesis first described in general α, β followed by five (1—5)-typical examples which clearly show the conditions under which the experiments were carried out.

The formulae, molecular weight, m. p. and the analytical data summarized in tables (1—3).

Experimental

1, 2, 3, 4-tetrahydronaphthylamine-1 (4) was prepared from α -tetralon-oxime. This was produced from α -tetralone and $\text{NH}_2\text{OH} \cdot \text{HCl}$ in the presence of KOH in MeOH by refluxing. The oxime is then reduced by Na in ethanol to give the amine.

Cyclohexylamine (5) was produced from cyclohexanone-oxime reducing with Na in ethanol.

Cyclopentylamine (6) was obtained in the same way.

Chloro-acetic acid chloride was prepared from monochloroacetic acid with PCl_3 and the end product distilled.

Chloro-propionic acid chloride (7) was prepared from acrylonitrile with conc. HCl . First β -chloro-propionic acid was obtained then chlorinated with PCl_3 and the product distilled.

The preparation of chlorocarbonic acid amides (III).

(General description) (see reaction a) 0,1 mol of amine is dissolved in 200 ml dry benzene adding to it 0,1 mol of triethyl-amine constantly stirring it for about 30 minutes while dropping constantly 0,1 mol chlorocarbonic acid chloride dissolved in 100 ml of dry benzene. Thereafter the mixture is refluxed for 30 minutes, in water bath, then the crystals of the triethylamine-hydrochloride were filtered from the not wholly cooled mixture.

Table I

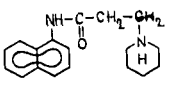
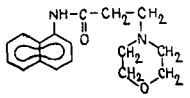
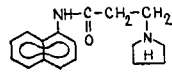
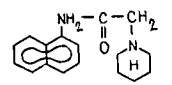
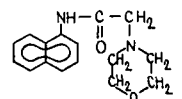
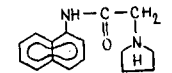
| Names of substances | Summary form | | M. w. | Physical data mp., bp., etc. | Calculated | | | | Found | | | |
|---|--------------|------------------------|--------|------------------------------|------------|------|-------|-------|-------|------|-------|-------|
| | | | | | C% | H% | N% | Cl% | C% | H% | N% | Cl% |
|  | Base | $C_{18}H_{22}N_2O$ | 282,37 | 90—91 | — | — | — | — | — | — | — | — |
| | HCl | $C_{18}H_{23}N_2OCl$ | 318,84 | 208—209 | 67,80 | 7,27 | 8,78 | 11,12 | 67,78 | 7,20 | 8,80 | 11,30 |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{17}H_{21}N_2O_2Cl$ | 320,83 | 230—231 | 63,64 | 6,59 | 8,73 | 11,05 | 64,30 | 6,82 | 8,78 | 9,34 |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{17}H_{21}N_2OCl$ | 304,83 | 208—209 | 66,98 | 6,94 | 9,19 | 11,63 | 67,10 | 7,19 | 9,03 | 9,92 |
|  | Base | $C_{17}H_{20}N_2O$ | 268,35 | 118 | 76,08 | 7,51 | 10,44 | — | 75,13 | 7,87 | 10,31 | |
| | HCl | $C_{17}H_{21}N_2OCl$ | 304,81 | 215 | 66,98 | 6,94 | 9,19 | 11,63 | 67,10 | 7,02 | 8,9 | 11,60 |
|  | Base | $C_{16}H_{18}N_2O_2$ | 270,32 | 106 | 71,08 | 6,71 | 10,36 | — | 71,33 | 6,98 | 9,67 | |
| | HCl | $C_{16}H_{19}N_2O_2Cl$ | 306,64 | 235 | 62,63 | 6,24 | 9,13 | 12,10 | | | | |
|  | Base | $C_{16}H_{18}N_2O$ | 254,32 | 108—109 | 75,55 | 7,13 | 11,01 | — | 74,02 | 7,06 | 10,90 | |
| | HCl | $C_{16}H_{19}N_2OCl$ | 290,79 | 219—221 | 66,08 | 6,58 | 9,63 | 12,19 | | | | |

Table II.

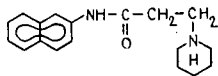
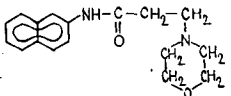
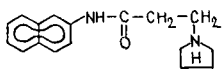
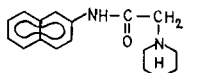
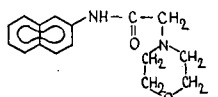
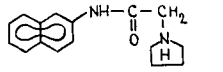
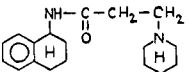
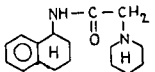
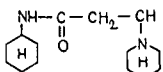
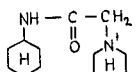
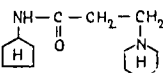
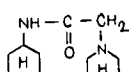
| Names of substances | Summary form | | M. w. | Physical data mp., bp., etc. | Analytical dates | | | | | | | |
|---|--------------|------------------------|--------|------------------------------|------------------|------|------|-------|-------|------|------|-------|
| | | | | | Calculated | | | | Found | | | |
| | | | | | C | H | N | Cl | C | H | N | Cl |
|  | Base | $C_{18}H_{22}N_2O$ | 282,37 | 90—91° | — | — | — | — | — | — | — | — |
| | HCl | $C_{18}H_{23}N_2OCl$ | 318,84 | 219—220 | 67,90 | 7,27 | 8,78 | 11,12 | 67,77 | 7,54 | 8,73 | 10,86 |
|  | Base | $C_{17}H_{20}N_2O_2$ | 284,36 | 87—88 | — | — | — | — | — | — | — | — |
| | HCl | $C_{17}H_{21}N_2O_2Cl$ | 320,83 | 255—256 | 63,64 | 6,59 | 8,73 | 11,05 | 63,56 | 6,96 | 8,42 | 10,91 |
|  | Base | $C_{17}H_{20}N_2O$ | 768,46 | 91—92 | — | — | — | — | — | — | — | — |
| | HCl | $C_{17}H_{21}N_2OCl$ | 304,83 | 208—210 | 66,98 | 6,94 | 9,19 | 11,63 | 67,10 | 7,79 | 8,88 | 11,57 |
|  | Base | $C_{17}H_{20}N_2O$ | 268,46 | 89—90 | — | — | — | — | — | — | — | — |
| | HCl | $C_{17}H_{21}N_2OCl$ | 304,83 | 242—244 | 66,98 | 6,94 | 9,19 | 11,63 | 67,63 | 7,07 | 9,08 | 11,30 |
|  | Base | $C_{16}H_{18}N_2O_2$ | 270,33 | 90—91 | — | — | — | — | — | — | — | — |
| | HCl | $C_{16}H_{19}N_2O_2Cl$ | 306,80 | 235—237 | 62,63 | 6,24 | 9,13 | 12,10 | 62,72 | 6,45 | 8,91 | 11,51 |
|  | Base | $C_{16}H_{18}N_2O$ | 254,33 | 100—101 | — | — | — | — | — | — | — | — |
| | HCl | $C_{16}H_{19}N_2OCl$ | 290,80 | 236—237 | 66,08 | 6,58 | 9,63 | 12,19 | 65,57 | 6,66 | 9,54 | 11,45 |

Table III.

| Names of substances | Summary form | | M. w. | Physical data mp., bp., etc. | Calculated | | | | Found | | | |
|---|--------------|----------------------|---------|------------------------------|------------|------|-------|-------|-------|-------|-------|-------|
| | | | | | C% | H% | N% | Hlg% | C% | H% | N% | Hlg% |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{18}H_{27}N_2OCl$ | 322,876 | 175 | 66,95 | 8,43 | 8,67 | 10,98 | 66,38 | 9,08 | 7,36 | 10,81 |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{17}H_{25}N_2OCl$ | 308,846 | 182—183 | 66,11 | 8,15 | 9,07 | 11,74 | 65,93 | 8,04 | 9,08 | 11,17 |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{14}H_{27}N_2OCl$ | 274,836 | 188 | 61,19 | 9,90 | 10,19 | 12,90 | 60,36 | 10,43 | 9,84 | 12,46 |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{13}H_{25}N_2OCl$ | 260,806 | 166 | 59,86 | 9,66 | 10,74 | 13,59 | 59,80 | 9,80 | 10,90 | 13,75 |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{13}H_{25}N_2OCl$ | 260,806 | 168—170 | 59,86 | 9,66 | 10,74 | 13,59 | 59,07 | 10,15 | 9,89 | 13,13 |
|  | Base | | | | | | | | | | | |
| | HCl | $C_{12}H_{23}N_2OCl$ | 246,776 | 164 | 58,40 | 9,39 | 11,35 | 14,37 | 58,30 | 9,75 | 11,20 | 14,12 |

The benzene filtrate was used for the next step, without isolation of III.

The further condensation of chlorocarbonic acid amide with piperidine or other secondary amines respectively. To obtain V.

(General description) (see reaction b)

The benzene solution obtained from step α was reduced in vacuum to 50 ml, then add 0,2 mol piperidine or other secondary bases to it.

The mixture as a rule was strongly warmed, few minutes after, crystals were separated. Refluxed it in water bath for 1 hour. After cooling the crystals were filtered, washed several times with water to remove the unchanged secondary base. Dried over anhydrous, evaporated, and the basic residue may be recrystallised from acetone if need be.

Dissolving the bases in acetone and acidified it by absolute alcoholic hydrochloride (about 20–25%) to acidic pH. Keep it in cold. Having filtered the crystals when needed recrystallized from absolute ethanol, aqueous ethanol, mixture of acetone-ethanol or only from acetone.

(It should be mentioned that the above generally described method refers to the substances listed in the tables. Only some typical examples will be emphasized.)

Example 1.

β -(1-piperidino)-propionic acid- α -naphthylamide-HCl.

28,6 g (0,2 mol of α -naphthyl-amine was dissolved in 200 ml of dry benzene in a 500 ml three necked round flash provided with stirrer, condenser and a dropping funnel. 20,2 g (0,2 mol) of triethylamine was added to it and dropping in 25,4 g (0,2 mol) β -chloro-propionic acid chloride dissolved in 50 ml of dry benzene, the solution stirred slowly and constantly (about 30 minutes). Following the dropping the reaction mixture is then refluxed for an other 30 minutes. Cooled it to about 40–50 °C and the triethylamine-HCl is filtered. The benzene filtrate is reduced to about 200 ml in vacuum and while skaking 34 g (0,4 mol) of piperidine was added in small portions. After the vigorous reactions, the mixture was refluxed for 30 minutes. Than it was cooled and the piperidine-HCl was filtered, then the filtrate diluted with benzene and washed several times with water to remove the unchanged piperidine. Having dried the benzene solution (anhydrous Na_2SO_4) the benzene was evaporated and the dense oily residue dissolved in about 10 ml acetone. After cooling it was rubbed as long as the crystallization was started. Keaped in a refrigerator at night then filtered and the precipitate was washed with a small amount of cold acetone.

The weight of the product: 28,3 g (yield 50,2% calculated on α -naphthylamine). Mp.: 87–89 °C.

By recrystallization from about 10 ml acetone the substance weight: 22,6, mp.: 90–91 °C.

The recrystallized pure base (22,6 g) was dissolved in 500 ml of hot acetone thereafter the calculated amount of absolute alcoholic HCl (about 20–30%) was dropped meanwhile shaking the solution. Keeping it in refrigerator. The praecipitate was filtered and washed with absolute alcohol. Weight: 25,2 g. Yield: 92,2%; mp.: 208–209 °C (decomp.). Recrystallized again from 85% ethanol the m. p. is

unchanged. The weight will be: 22,0 g. (It is to be noted, that the bases were mostly obtained as HCl salt without isolation of the free base.)

Example 2.

1-(piperidino) acetic acid- α -naphthylamide-HCl.

14,3 g (0,1 mol) of α -naphthylamine was dissolved in 500 ml dry benzene in a 1000 ml round-bottom three-necked flask supplied with stirrer, condenser and with a dropping-funnel. Adding 10,1 g (0,1 mol) triethylamine, then 11,3 g (0,1 mol) chloroacetic acid chloride dissolved in 200 ml of dry benzene being dropped (about 30 minutes) while constantly stirring the mixture.

The mixture was refluxed for 30 minutes after having dropped the acid chloride the triethylamine-HCl was separated from the solution. The benzene solution was evaporated to about 40–80 ml and 17 g of piperidine solution were added. The mixture was heated for 30 minutes after the intensive reaction. Thereafter the piperidine-HCl was filtered and the solution was diluted with water and washed in order to remove the piperidine HCl residue. (The coloured solution was always successfully purified with 20% of HCl. The basis were released with Na_2CO_3 from the acidic solution. The base was extracted from the basic solution with benzene. It was dried (anhydrous Na_2SO_4). The benzene solution was filtered, evaporated and the residue was recrystallized from acetone. The weight of the base: 16,5 g (Yield: 61,5% calculated on naphthylamide-1) m. p.: 118 °C. The hydrochloride was prepared from the acetone solution of the base with the calculated amount of alcoholic HCl. Kept in a refrigerator for a night. The obtained crystals were filtered, washed with absolute ethanol. Weight: 17,5 g (Yield: 96,4%). It could be recrystallized from 85% ethanol. M. p.: 215 °C.

Example 3.

β -(1-piperidino)-propionic acid- α -1, 2, 3, 4-tetrahydronaphthyl-amine-HCl.

14,7 g (0,1 mol) of 1, 2, 3, 4-tetrahydro- α -naphthylamine was dissolved in 100 ml of dry benzene in a 500 ml round bottomed three-necked flask provided with a stirrer condenser and a dropping-funnel. 10,1 g (0,1 mol) triethylamine, then 12,6 g (0,1 mol) β -chloro-propionic acid chlorides dissolved in 100 ml of dry benzene for 30 minutes. Refluxed it for about 30 minutes, filter the triethylamine-HCl crystals while hot. The benzene solution was then evaporated to about 50 ml in vacuum. 17 g of piperidine was added and refluxed after the strong reaction for about 30 minutes. The piperidine-HCl was filtered and the solution washed in the same way as described above. It was dried (anhydrous Na_2SO_4). Filtered and the solution evaporated in vacuum. The residue was dissolved in acetone and the calculated amount of alcoholic HCl was added, kept in a refrigerator for the night. The crystals were filtered and washed with absolute ethanol. Weight: 30,2 g (Yield: 93% calculated of 1, 2, 3, 4-tetrahydro- α -naphthylamine.). It can be recrystallized from absolute ethanol if needed. Mp.: 175 °C.

Example 4. *β -(1-piperidino)-propionic acid cyclohexylamine-HCl.*

9,9 (0,1 mol) of cyclohexylamine was dissolved in 100 ml of dry benzene and 10,1 g (0,1 mol) of triethylamine was added in a 250 ml three necked flask provided as described above. Dropping into the flask 12,6 g (6,1 mol) of β -chloro-propionic acid chloride dissolved in 50 ml of dry benzene. The procedure is exactly the same as described in example 3.

The obtained weight of HCl was 18,5 g (Yield: 67,5% calculated for cyclohexylamine).

Recrystallized from absolute ethanol, m. p.: 188 °C.

*Example 5.**(1-piperidino)-acetic acid-cyclopentylamine-HCl.*

8,5 g (0,1 mol) of cyclopentylamine was solved in 100 ml of dry benzene and 10,1 g (0,1 mol) of triethylamine was added in a 250 ml three necked flask provided as described above. Dropping 11,2 g (0,1 mol) of chloroacetic acid chloride for 30 minutes.

The procedure is alike that described in the other examples.

The benzene solution was extracted with dilute HCl and the benzene phase containing contaminations was separated. The acidic solution alcalized with Na_2CO_3 and extracted again with benzene. The dried benzene solution (anhydrous Na_2SO_4) evaporated and the basic residue was dissolved in acetone and the HCl salt formed with the calculated amount of alcoholic HCl. Keeping in refrigerator at night. The obtained crystals were filtered and washed with acetone. Weight: 12,6 g (Yield: 51,2% calculated for cyclopentylamine). Recrystallized from a mixture of absolute alcohol and acetone.

M. p.: 164 °C.

* * *

We wish to express our thanks to Mr. J. FÜLÖP and Dr. J. FISZTER for their valuable assistance and our indebtedness for the analysis to our Analytical Laboratory and to „Gedeon Richter Pharmaceutical Works, Budapest” for their kind support.

The detailed pharmacological examinations will be published elsewhere.

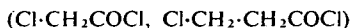
**ИЗУЧЕНИЯ ДЕЙСТВИЯ МЕЖДУ ФИЗИОЛОГИЧЕСКИМИ И ХИМИЧЕСКИМИ
СТРОЕНИЯМИ ВЕЩЕСТВ, ДЕЙСТВУЮЩИХ НА ЦЕНТРАЛЬНЫЙ
НЕРВНЫЙ МОЗГ. VII**

*Синтез ароматических и гомоциклических терциер-аминоацетиллов
и пропионил-производных*

Й. Лазар, Б. Маткович, Ш. Фельдак, Й. Порсас

Уже перед рассмотрениями было известно, что аминокислоты в центральной нервной системе вызывают депрессию. Поэтому были произведены рассмотрения в группе аминокислот для взаимной зависимости действия и строения.

Публикация занимается конденсацией нафтиламинов и разных гомоциклических аминов, возникшей при действии клоралкилхлорангидрида



и разных вторичных аминов. Для полученных соединений изучалась роль дальности метилена и разных оснований на фармакологическое действие. Между рассмотренными соединениями нашлись многочисленные соединения антиникотинного действия местного анестетика.

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STABILITY AND STRUCTURAL PROPERTIES OF ORGANOSUSPENSIONS. II

Stability of Organophilic Bentonite Suspensions in Mixtures of Apolar and Polar Liquids

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The sedimentation rates and sediment volumes of suspensions of "Bentone 34" were investigated in mixtures of benzene with methanol, ethanol, propanol and butanol, further with nitrobenzene. The sedimentation rates proved to change with alcohol concentrations according to a curve of minimum-maximum type. In the first and particularly in the third extreme points the formation of almost thixotropic systems was experienced. At maximum sedimentation rates a diffuse sedimentation takes place. Changes in sediment volume and sedimentation rate are always of opposite sense. The thixotropic trend diminishes with the rise of the number of carbon atoms in the alcohol. This was interpreted by the Wo. OSTWALD—BUZÁGH principle of continuity. The formation of a structure sedimenting with a sharp boundary was experienced also in mixtures of benzene and nitrobenzene, up to certain limits of concentration. However, owing to specific solvation effect of nitrobenzene, the structure decomposes already over relatively low concentration of nitrobenzene, and a stable sol forms.

On this basis, the sedimentation and the structural properties of organophilic bentonite suspensions were interpreted by the disintegration of the particles and by the formation of a card skeleton structure of the evolved lamellae. On increasing the solvation, first a disintegration-adhesion (coherent), then an incoherent section follows. Subsequently, in the case of alcohols coagulation and structure formation (second coherent section), and lastly a structureless coarse coagulation take place.

Introduction. In our experiments with pure organic liquids described in our previous communication [1] we established that the card skeleton theory of HOFMANN [2] can also be applied to organophilic clay minerals, and that the stability and sediment volume are determined by the disintegration of the particles and the adhesion forces existing between the lamellae [3]. In order to study more thoroughly the role of solvation conditions, measurements of sedimentation rate and sediment volume were carried out also in mixtures of apolar and polar organic solvents such as benzene and methanol, benzene and ethanol, benzene and propanol, benzene and butanol, further benzene and nitrobenzene.

The applied technique was identical in every respect with that used in our earlier experiments [1], "Dutch Boy Bentone 34" serving as basic substance. The investigations were carried out with 0,2 g samples in 20 ml test tubes with 0,1 ml scale, in a thermostat at a temperature of $25 \pm 0,1^\circ\text{C}$.

Experimental results

In mixtures of benzene and ethanol of various composition, just as in various pure organic solvents, sedimentation with a diffuse and sharp boundary surface

Table I
Sedimentation rate and sediment volume vs. concentration by volume of methanol

| Methanol volume proc. | Methanol mol/l. | Dielectric const. at 25°C | Sedimentation rate cm/sec. | Sediment volume ml |
|-----------------------|-----------------|---------------------------|----------------------------|--------------------|
| 0,00 | 0,00 | 2,29 | 0,0057 | 4,10 |
| 0,50 | 0,09 | 2,32 | 0,0038 | 5,40 |
| 1,00 | 0,17 | 2,35 | 0,0024 | 5,50 |
| 1,75 | 0,30 | 2,41 | 0,0010 | 7,00 |
| 2,50 | 0,43 | 2,47 | 0,0014 | 6,20 |
| 5,00 | 0,85 | 2,66 | 0,0031 | 5,00 |
| 7,50 | 1,28 | 2,88 | 0,0111 | 3,40 |
| 10,00 | 1,70 | 3,16 | 0,0145 | 2,60 |
| 12,50 | 2,13 | 3,36 | 0,0160 | 2,40 |
| 15,00 | 2,56 | 3,83 | 0,0135 | 2,70 |
| 20,00 | 3,41 | 4,47 | 0,0050 | 4,80 |
| 25,00 | 4,26 | 5,73 | 0,0044 | 5,10 |
| 30,00 | 5,11 | 6,84 | 0,0042 | 4,10 |
| 45,00 | 7,67 | 10,70 | 0,0086 | 2,80 |
| 60,00 | 10,22 | 14,92 | 0,0144 | 2,15 |
| 100,00 | 17,04 | 25,49 | 0,0434 | 1,20 |

Table II
Sedimentation rate and sediment volume vs. concentration by volume of ethanol

| Ethanol volume proc. | Ethanol mol/l. | Dielectric const. at 25°C | Sedimentation rate cm/sec. | Sediment volume ml |
|----------------------|----------------|---------------------------|----------------------------|--------------------|
| 0,00 | 0,00 | 2,29 | 0,0057 | 4,10 |
| 0,25 | 0,06 | 2,36 | 0,0042 | 5,60 |
| 0,50 | 0,12 | 2,44 | 0,0003 | 7,80 |
| 1,00 | 0,25 | 2,48 | 0,0003 | 8,00 |
| 2,50 | 0,61 | 2,66 | 0,0011 | 7,20 |
| 5,00 | 1,23 | 3,00 | 0,0031 | 3,20 |
| 7,50 | 1,83 | 3,36 | 0,0082 | 2,90 |
| 10,00 | 2,46 | 3,82 | 0,00006 | 9,50 |
| 15,00 | 3,68 | 5,01 | 0,00003 | 10,10 |
| 20,00 | 4,91 | 6,30 | 0,00004 | 7,10 |
| 30,00 | 7,37 | 9,56 | 0,0022 | 4,30 |
| 45,00 | 11,05 | 14,70 | 0,0191 | 2,50 |
| 60,00 | 14,73 | 20,22 | 0,0580 | 1,70 |
| 100,00 | 24,55 | 33,56 | 0,1190 | 0,85 |

Table III
Sedimentation rate and sediment volume vs. concentration by volume of propanol

| Propanol volume proc. | Propanol mol/l. | Dielectric const. at 25°C | Sedimentation rate cm/sec. | Sediment volume ml |
|-----------------------|-----------------|---------------------------|----------------------------|--------------------|
| 0,00 | 0,00 | 2,29 | 0,0057 | 4,10 |
| 0,50 | 0,07 | 2,32 | 0,0045 | 4,80 |
| 1,00 | 0,13 | 2,35 | 0,0036 | 5,00 |
| 2,50 | 0,33 | 2,46 | 0,0033 | 5,60 |
| 5,00 | 0,67 | 2,57 | 0,0042 | 4,90 |
| 7,50 | 1,00 | 2,73 | 0,0057 | 4,10 |
| 10,00 | 1,33 | 2,90 | 0,0111 | 3,40 |
| 15,00 | 2,00 | 3,33 | 0,0187 | 2,60 |
| 20,00 | 2,66 | 3,82 | 0,0134 | 3,10 |
| 22,00 | 2,93 | 4,11 | 0,0120 | 3,20 |
| 25,00 | 3,33 | 4,55 | 0,0104 | 3,25 |
| 30,00 | 4,00 | 5,33 | 0,0104 | 3,30 |
| 40,00 | 5,32 | 7,28 | 0,0072 | 4,00 |
| 45,00 | 5,99 | 8,22 | 0,0055 | 4,10 |
| 50,00 | 6,66 | 9,36 | 0,0058 | 3,30 |
| 60,00 | 7,99 | 12,81 | 0,0084 | 2,30 |
| 80,00 | 10,65 | 16,64 | 0,0138 | 1,50 |
| 100,00 | 13,31 | 21,08 | 0,0162 | 1,00 |

Table IV
Sedimentation rate and sediment volume vs. concentration by volume of butanol

| Butanol volume proc. | Butanol mol/l. | Dielectric const. at 25°C | Sedimentation rate cm/sec. | Sediment volume ml |
|----------------------|----------------|---------------------------|----------------------------|--------------------|
| 0,00 | 0,00 | 2,29 | 0,0057 | 4,10 |
| 1,00 | 0,11 | 2,35 | 0,0058 | 4,80 |
| 2,00 | 0,22 | 2,40 | 0,0067 | 4,40 |
| 3,00 | 0,33 | 2,45 | 0,0083 | 3,70 |
| 6,00 | 0,63 | 2,60 | diffuse | 3,20 |
| 10,00 | 1,09 | 2,85 | „ | 2,40 |
| 15,00 | 1,63 | 3,15 | „ | 2,30 |
| 20,00 | 2,16 | 3,56 | „ | 2,10 |
| 30,00 | 3,27 | 4,54 | „ | 2,10 |
| 40,00 | 4,35 | 5,94 | „ | 2,10 |
| 50,00 | 5,44 | 7,72 | „ | 1,80 |
| 65,00 | 7,07 | 10,76 | „ | 1,60 |
| 80,00 | 8,70 | 14,01 | „ | 1,20 |
| 100,00 | 10,87 | 17,85 | „ | 0,70 |

was experienced. The values of sedimentation rate and sediment volume measured in various mixtures are given in Tables I—IV. It must be noted that, according to our measurements, the differences due to changes in the density and inner friction of liquids proved to be negligible in respect to the experienced effects. The sedimentation rates and sediment volumes plotted against concentrations by volume of the alcohols are shown in Figures 1—4 while the sedimentation rates plotted against the molar concentrations of alcohols in Fig. 5.

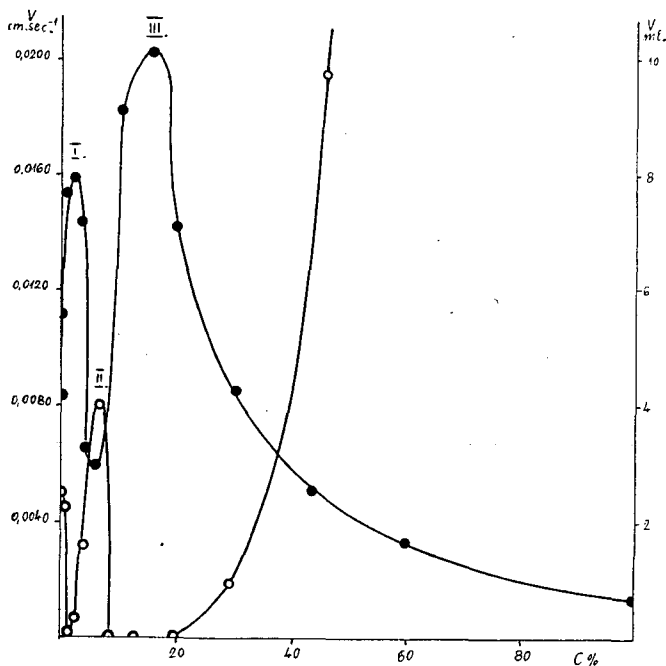


Fig. 1. Sedimentation rate and sediment volume vs. concentration by volume of methanol.

○ sedimentation rate
● sediment volume

It can be seen from the data of the tables and from the figures that three extreme points appear in the changes of sedimentation rate and sediment volume in the mixtures of benzene with methanol, ethanol and propanol. Changes in sedimentation rate and sediment volume always proved to be opposite to each other.

Up to the first extreme point (*cf.* point I in the figures) the capability of structure formation of the suspensions gradually increased (first coherent section). Accordingly, the sedimentation rates diminished while at the same time the sediment volumes increased. The "quasi-thixotropic" character and apparent stability, respectively, attained their maximum values in the first critical point.

In the next section of the curve (between critical points I and II) the capability of structure formation decreased (incoherent section). The sedimenting suspension

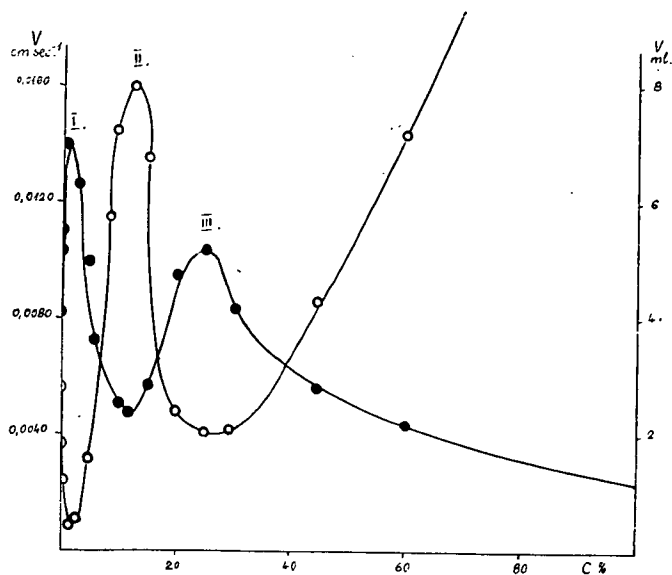


Fig. 2. Sedimentation rate and sediment volume vs. concentration by volume of ethanol.
 ○ sedimentation rate ● sediment volume

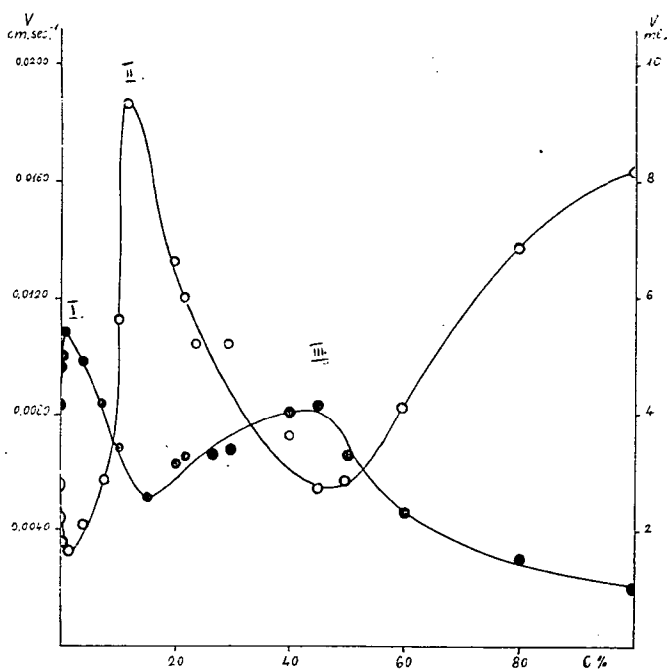


Fig. 3. Sedimentation rate and sediment volume vs. concentration by volume of propanol.
 ○ sedimentation rate ● sediment volume

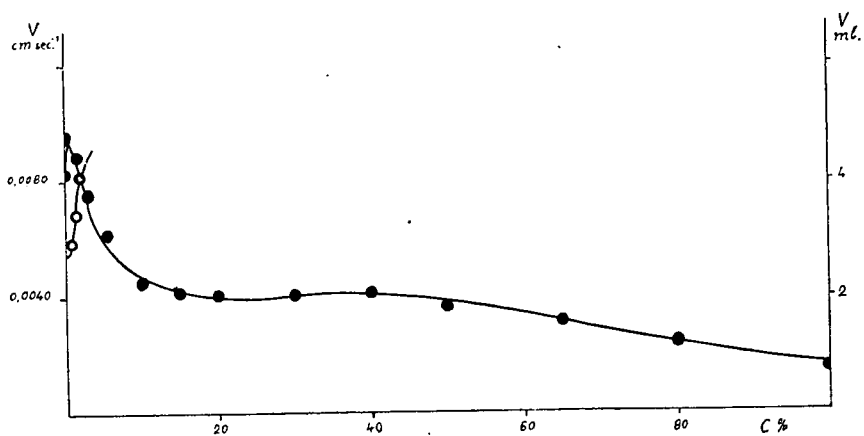


Fig. 4. Sedimentation rate and sediment volume vs. concentration by volume of butanol.

○ sedimentation rate
● sediment volume

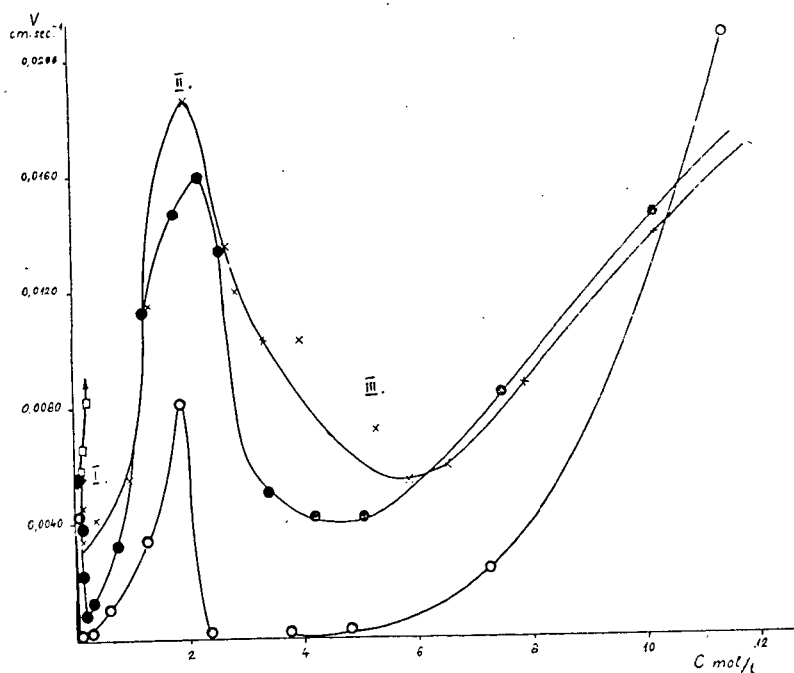


Fig. 5. Sedimentation rates vs. the molar concentrations of alcohols.

○ methanol
● ethanol
× propanol
□ butanol

becomes to be of a more diffuse distribution when the concentration of alcohols rises, and the particles sediment more or less independently of each other. Accordingly, the sedimentation rate increases and the sediment volume diminishes. Minimum values of the quasi thixotropic character and of apparent stability appear in critical point II (cf. points II in the figures). Subsequently, the trend to thixotropy again increases (second coherent section). Thus, sedimentation takes place with a sharp boundary surface and at gradually decreasing rates. Sediment volumes again rise. Quasi thixotropic character and apparent stability attain their second maxima in point III. At this second maximum, the sedimentation rate is much lower than at the first maximum. Moreover, the systems proved to be almost thixotropic.

Above the third critical concentration (coagulation section), coarse aggregates can be observed already at the preparation of the suspensions. The sedimentation is of a diffuse character, sedimentation rates rapidly rise while sediment volumes decrease on raising the concentration of alcohol.

The above described qualitative observations in respect to the behaviour of suspensions are summarised in Table V.

Table V
Behaviour of suspensions in various sections of the curves sedimentation rate vs. alcohol concentration

| Sections | Interaction with medium | Character of sedimentation | Character of sediment |
|---------------------------|--|--|---|
| up to point I | Increase of swelling, disintegration. Peptised particles form a coherent, loose structure. | with a sharp boundary | Transparent, swollen, loose, easily suspendable |
| between points I and II | Strong swelling, peptisation. Adhesion forces diminish with increasing alcohol concentrations. | diffuse | Compact, transparent jelly With the increase of alcohol concentration its suspendability gradually decreases. Low sediment volumes. |
| between points II and III | Aggregation of peptised particles increases with increasing alcohol concentrations. | With increasing alcohol concentrations boundary surfaces become sharper. | Opaque, loose, readily suspendable. High sediment volumes. |
| beyond point III | Strong coagulation already on preparing the suspension. | diffuse | Readily suspendable. Sediment volume low. |

On comparing the curves of sedimentation rates in mixtures containing alcohols with various numbers of carbon atom, it appears that the quasi thixotropic character of systems corresponding to critical concentrations I and III is affected to a great extent by the number of carbon atoms of the applied alcohol, in that this character becomes weaker with the rise of the number of carbon atoms. The increase of the diffuse character with the rise of the number of carbon atoms is readily observable qualitatively in the section between critical concentrations I and II (incoherent section).

In mixtures of benzene and butanol, up to a butanol content of 3%, sedimentation takes place with a sharp boundary surface. At butanol concentrations over 3%, however, owing to the strong peptising effect of butanol, a solvent with a relatively high number of carbon atoms, sedimentation is rather diffuse. Therefore, it was not possible to quantitatively investigate sedimentation rates with the method applied by us. However, it has been qualitatively established that at high concentrations of alcohol (over 80%) the coagulating effect of alcohols also prevails in this case, though to a smaller extent than in the case of alcohols with a lower number of carbon atoms.

In the case of mixtures containing methanol, ethanol and propanol, also the dielectric constants were determined in media of various composition (cf. Fig. 6).

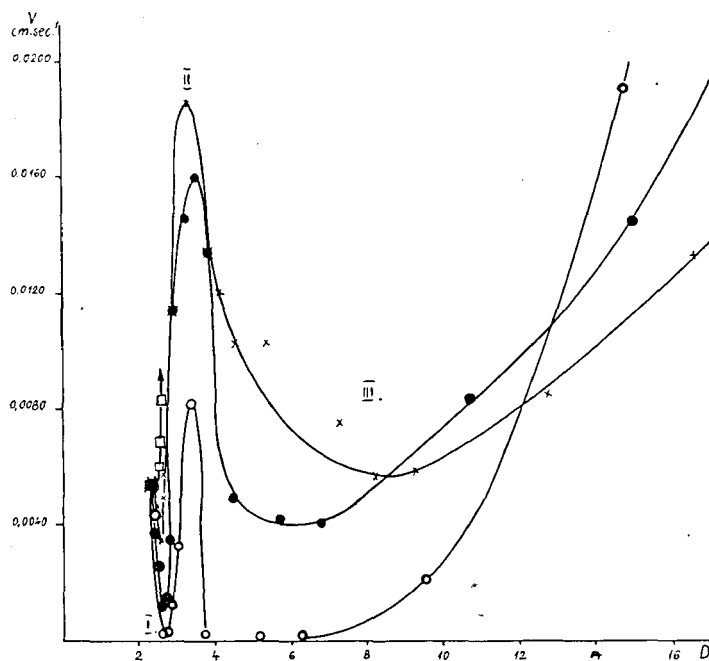


Fig. 6. Sedimentation rates vs. dielectric constant of the mixtures.

- methanol
- ethanol
- × propanol
- butanol

On comparing the measured dielectric constants of mixtures of critical composition (cf. Table VI) it can be observed that the first and second critical points of the curves appear practically at the same dielectric constants in the case of all the three types of alcohols tested. The critical point III, in turn, occurs in the case of alcohols with a rising number of carbon atoms at increasing values of dielectric constant.

Table VI
Dielectric constants at the critical points

| | I | II | III |
|----------------|------|------|------|
| Methanol | 2,48 | 3,36 | 5,01 |
| Ethanol | 2,41 | 3,36 | 5,73 |
| Propanol | 2,46 | 3,33 | 8,22 |

In mixtures of benzene and nitrobenzene, sedimentation rates could only be measured up to a nitrobenzene content of 30%. In mixtures containing more than 30% of nitrobenzene, suspensions were obtained which sedimented in a diffuse manner, and thus it was impossible to quantitatively establish sedimentation rates with the applied method. The measured values of sedimentation rate and sediment volume are shown in Table VII and Fig. 7, respectively.

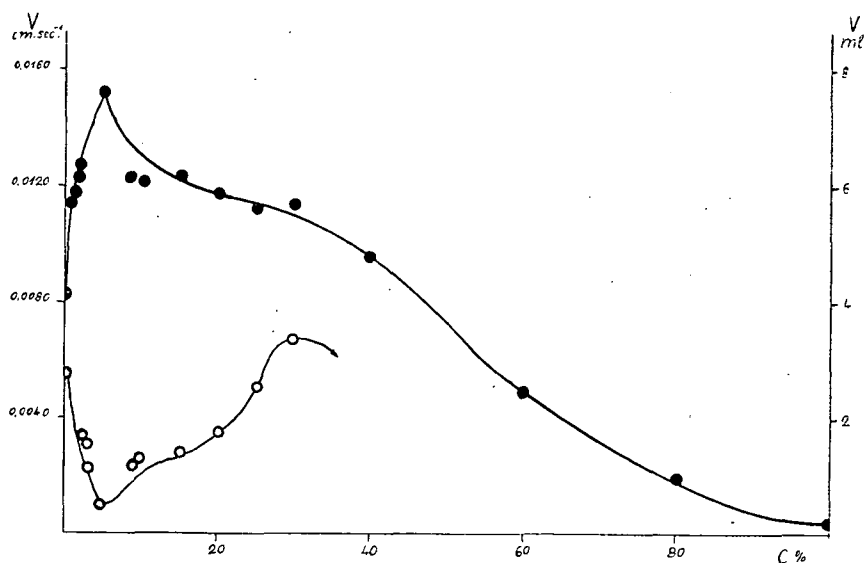


Fig. 7. Sedimentation rate and sediment volume vs. concentration by volume of nitrobenzene.
○ sedimentation rate
● sediment volume

On increasing the quantity of nitrobenzene, similarly a system of quasi thixotropic character formed in these mixtures, up to certain limit of concentration (coherent section). Accordingly, sedimentation took place with a sharp boundary surface, sedimentation rates decreased while sediment volumes increased. Over this concentration limit, the structure decomposed, gradually increasing proportions of the substance peptised and sediment volumes diminished (stable incoherent system).

Table VII

Sedimentation rate and sediment volume vs concentration by volume of nitrobenzene

| Nitrobenzene volume proc. | Dielectric const. at 25 °C | Sedimentation rate cm/sec. | Sediment volume ml |
|---------------------------------|----------------------------------|-------------------------------|--------------------------|
| 0,00 | 2,29 | 0,0057 | 4,10 |
| 0,25 | 2,46 | 0,0033 | 5,60 |
| 0,50 | 2,47 | 0,0029 | 5,70 |
| 1,00 | 2,77 | 0,0026 | 6,20 |
| 2,50 | 2,94 | 0,0022 | 6,30 |
| 5,00 | 3,53 | 0,0010 | 7,60 |
| 7,50 | 3,93 | 0,0022 | 6,20 |
| 10,00 | 4,48 | 0,0024 | 6,10 |
| 15,00 | 5,70 | 0,0027 | 6,20 |
| 20,00 | 6,93 | 0,0035 | 5,70 |
| 25,00 | 8,17 | 0,0051 | 5,50 |
| 30,00 | 9,54 | 0,0067 | 5,60 |
| 40,00 | 12,29 | diffuse | 4,70 |
| 60,00 | 15,97 | " | 2,50 |
| 80,00 | 25,67 | " | 1,00 |
| 100,00 | 34,82 | " | 0,30 |

Evaluation of experimental results

Our earlier statements concerning pure liquids [1] were supported by the experimental data obtained with liquid mixtures.

In benzene, the particles of the organophilic bentonite powder disintegrate, due to fair swelling. In this way, the coarse isodimensional particles convert into a greater number of lamellar units. Since however the polar portions of surfaces (4) are poorly solvated by benzene, relatively great adhesive forces form between these. Thus, the card skeleton structure develops from the lamellae, resulting in a relatively slow sedimentation with a sharp boundary surface.

On the effect of the small amounts of alcohol added to benzene, owing to the orientated adsorption of the alcohol molecules, the particles are disintegrated to a gradually increasing extent (cf. JORDAN [4]). However, the possibility of adhesive linkages still exists between the polar portions of surface not coated by alcohol molecules. Moreover, the capability of structure formation becomes stronger up to critical point I, due to the increase of the number of particles (first coherent section). Accordingly, the sedimentation rates decrease while, just owing to the increase of the number of particles, sediment volumes increase at the same time.

In the section after critical point I, the linkages between particles decompose, due to the now already complete solvation of the polar portions of surface (incoherent section). Sedimentation takes up a diffuse character, just due to the decomposition of structure, and thus the sedimentation rates increase up to critical point II. From systems sedimentating in this manner, a sediment consisting of swollen particles but of compact nature is deposited.

On further raising the quantities of alcohol added, the polar character of the medium becomes predominant. Consequently, the continuous transition (continuity) between the organophilic bentonite particles of apolar surface and the medium

decreases, and thus the system coagulates (*cf.* the WO. OSTWALD—BUZÁGH principle of continuity [5]). Accordingly, the particles again form a structure (second coherent section), a quasi thixotropic character evolves, and sedimentation rates decrease. The sediment again takes up a looser aggregational state, while the sediment volumes increase. This becomes gradually more pregnant up to critical point III where sedimentation rates disclose again a minimum, and sediment volumes a maximum value. On further raising the concentration of alcohol, the medium becomes polar to such an extent that the powder is *a priori* not disintegrated. In this section, when the alcohol concentration is increased, gradually a more coarse coagulation takes place, without any structure formation. The sedimentation rate increases and the sediment volume decreases with the rise of alcohol concentration (coagulation section).

On investigating the role of the *dielectric constant* of the mixtures, the following statements can be made.

As it was mentioned earlier, in the case of all the three alcohols tested, both first critical points appear at the same dielectric constant while the site of critical point III shifts to mixtures of higher dielectric constants when the number of carbon atoms of the alcohol increases. This is interpreted as follows. The sites of critical points I and II are closely correlated with the orientated adsorption of alcohol molecules, and thus with the surface properties of the solvated substance, being practically independent of the number of carbon atoms of the alcohol present. Namely, from the aspect of the orientated adsorption of alcohols apparently only the relative quantities of polar portions of surface play significant role. The site of critical point III, in turn, is determined by the coagulating effect of alcohol, and thus it depends also on the number of carbon atoms of the alcohol. With the increase of the number of carbon atoms, the continuity between the apolar particle and the medium improves, and thus the coagulation effect becomes weaker [5].

Also the effect of alcohols with various numbers of carbon atom on the quasi thixotropic character can be explained by presuming that, with the increase of the number of carbon atoms, continuity improves and adhesion diminishes. Consequently, in the case of alcohols with higher numbers of carbon atoms a less rigid card skeleton structure evolve. Accordingly, with the increase of the number of carbon atoms, the height of the maximum of sediment volumes decreases.

In *mixtures of benzene and nitrobenzene*, when the content of nitrobenzene is raised, the solvation of particles and the continuity throughout increase because the organophilic bentonite is particularly well solvated by nitrobenzene [1, 4]. Up to a nitrobenzene content of 5%, linkages form between the lamellae, due to the adhesion of non completely solvated sites, and thus a card skeleton structure evolves. Accordingly, in this interval (coherent section) an increase of the number of particles and the formation of a quasi thixotropic character may be expected. At a nitrobenzene content of over 5%, the card skeleton structure already decomposes (*e. g.* beyond critical point I of the curve of alcohol), while the quantity of peptised portion increases, sedimentation becomes to be diffuse, and sediment volume diminishes. At nitrobenzene contents over 30% this solvation attains such an extent that a completely stable organophilic bentonite sol forms. Here the coagulating effect does not appear. Thus, the particular solvation-stabilisation effect of nitrobenzene manifests itself also in this case, and it cannot be explained by the polar

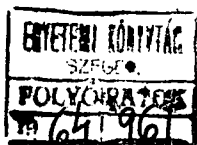
nature of nitrobenzene [4], because in the case of the similarly polar alcohols, coagulation takes place at the same dielectric constant. This also proves the correctness of our earlier presumption concerning specific adsorption [1].

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